

# **EXHIBIT A**

US006634961B2

(12) **United States Patent**  
**Higuchi et al.**(10) **Patent No.:** **US 6,634,961 B2**  
(45) **Date of Patent:** **\*Oct. 21, 2003**(54) **MULTI-PIECE SOLID GOLF BALL**(75) **Inventors:** **Hiroshi Higuchi, Chichibu (JP);**  
**Atsushi Nanba, Chichibu (JP)**(73) **Assignee:** **Bridgestone Sports Co., Ltd., Tokyo**  
**(JP)**(\*) **Notice:** Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.This patent is subject to a terminal dis-  
claimer.(21) **Appl. No.:** **10/156,950**(22) **Filed:** **May 30, 2002**(65) **Prior Publication Data**

US 2003/0017888 A1 Jan. 23, 2003

(30) **Foreign Application Priority Data**

May 30, 2001 (JP) ..... 2001-163238

(51) **Int. Cl.<sup>7</sup>** ..... **A63B 37/06**(52) **U.S. Cl.** ..... **473/357; 524/432**(58) **Field of Search** ..... **473/357, 356,**  
**473/359, 372, 374, 371, 373; 524/194,**  
**908, 432, 526, 534**(56) **References Cited****U.S. PATENT DOCUMENTS**4,683,257 A \* 7/1987 Kakiuchi et al. .... 473/372  
4,929,678 A \* 5/1990 Hamada et al. .... 525/193  
4,955,613 A \* 9/1990 Gendreau et al. .... 260/998.14  
5,252,652 A \* 10/1993 Egashira et al. .... 473/3725,733,205 A \* 3/1998 Higuchi et al. .... 473/373  
6,045,460 A \* 4/2000 Hayashi et al. .... 473/376  
6,194,505 B1 \* 2/2001 Sone et al. .... 473/371  
6,315,679 B1 \* 11/2001 Sano ..... 473/357**FOREIGN PATENT DOCUMENTS**EP 0 920 886 A2 6/1999  
GB 2 324 740 A 11/1998**OTHER PUBLICATIONS**M. R. Farrally, A. J. Cochran, "Science and Golf III", 1999,  
Human Kinetics, pp. 410, 412, 413.\*  
British Search Report, Oct. 17, 2002.

\* cited by examiner

*Primary Examiner*—Paul T. Sewell*Assistant Examiner*—Tom P Duong(74) *Attorney, Agent, or Firm*—Sughrue Mion, PLLC(57) **ABSTRACT**

In a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, the solid core is molded from a rubber composition comprising a base rubber composed of (a) 20–100 wt % of a polybutadiene having a high cis-1,4 content, a minimal 1,2 vinyl content and a viscosity  $\eta$  of up to 600 mPa·s at 25° C as a 5 wt % toluene solution, and satisfying a certain relationship between Mooney viscosity and polydispersity index in combination with (b) 0–80 wt % of another diene rubber, (c) an unsaturated carboxylic acid, (d) an organosulfur compound, (e) an inorganic filler, and (f) an organic peroxide; and the outer cover layer has a lower Shore D hardness than the inner cover layer. This combination of features gives the ball a good, soft feel upon impact and an excellent spin performance that provides increased distance.

**9 Claims, No Drawings**

US 6,634,961 B2

1

**MULTI-PIECE SOLID GOLF BALL****BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a multi-piece solid golf ball which has been imparted with a good, soft feel upon impact and an excellent spin performance that makes it possible to achieve an increased distance.

**2. Prior Art**

Various improvements are being made in formulating the polybutadiene used as the base rubber in golf balls so as to confer the balls with outstanding rebound characteristics.

For example, JP-A 62-89750 describes rubber compositions for use as the base rubber in solid golf balls, which compositions are arrived at by blending a polybutadiene having a Mooney viscosity of 70 to 100 and synthesized using a nickel or cobalt catalyst with another polybutadiene having a Mooney viscosity of 30 to 90 and synthesized using a lanthanide catalyst or polybutadiene having a Mooney viscosity of 20 to 50 and synthesized using a nickel or cobalt catalyst.

However, further improvements in the materials are required in the above art to achieve golf balls endowed with a good, soft feel upon impact and an excellent spin performance that helps increase the distance the ball travels when played.

JP-A 2-268778 describes golf balls molded using a blend composed of a polybutadiene having a Mooney viscosity of less than 50 and synthesized using a Group VIII catalyst in combination with a polybutadiene having a Mooney viscosity of less than 50 and synthesized with a lanthanide catalyst. However, golf balls with a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball cannot be obtained in this way.

The existing art also teaches multi-piece solid golf balls in which an intermediate layer is molded of a low-Mooney viscosity polybutadiene (JP-A 11-70187), solid golf balls molded from rubber compositions comprising a polybutadiene having a Mooney viscosity of 50 to 69 and synthesized using a nickel or cobalt catalyst in combination with a polybutadiene having a Mooney viscosity of 20 to 90 and synthesized using a lanthanide catalyst (JP-A 11-319148), solid golf balls molded from compositions based on a rubber having a 1,2 vinyl content of at most 2.0% and a weight-average molecular weight to number-average molecular weight ratio Mw/Mn of not more than 3.5 (JP-A 11-164912), golf balls molded from rubber compositions containing a high Mooney viscosity polybutadiene (JP-A 63-275356), and golf balls molded from rubber compositions comprising polybutadiene having a high number-average molecular weight in admixture with polybutadiene having a low number-average molecular weight (JP-A 3-151985). However, none of these prior-art golf balls truly have a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball.

Golf balls having a cover composed of a relatively hard inner layer and a relatively soft outer layer have already been disclosed in JP-A 6-218078, JP-A 6-343718, JP-A 7-24085, JP-A 9-239068, JP-A 10-151226, JP-A 10-201880, JP-A 11-104273, JP-A 11-104271, and Japanese Patent Applications No. 2000-274807 and 2000-274843. However, further improvements in distance are desired for the golf balls described in all of these specifications.

**SUMMARY OF THE INVENTION**

It is therefore an object of the present invention to provide multi-piece solid golf balls which are endowed with a good,

2

soft feel when hit with a golf club and an excellent spin performance that helps increase the distance traveled by the ball when played.

The inventor has discovered that golf balls having a solid core, an inner cover layer over the cover, and an outer cover layer over the inner cover layer, wherein the solid core is made of a rubber composition formulated from a particular type of base rubber combined in specific proportions with certain other materials, and the outer cover layer is softer than the inner cover layer, exhibit a good synergy from optimization of the solid core materials and an appropriate distribution of hardness between the inner and outer cover layers. Multi-piece solid golf balls thus constituted have a good, soft feel when hit with a golf club and an excellent spin performance that enables the ball to travel further when played.

Accordingly, the invention provides a multi-piece solid golf ball having a solid core, an inner cover layer enclosing the core, and an outer cover layer enclosing the inner cover layer. The solid core is molded from a rubber composition comprising 100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, and satisfying the relationship:  $10B + 5 \leq A \leq 10B + 60$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a). The rubber composition includes also (c) 10 to 60 parts by weight of an unsaturated carboxylic acid and/or a metal salt thereof, (d) 0.1 to 5 parts by weight of an organosulfur compound, (e) 5 to 80 parts by weight of an inorganic filler, and (f) 0.1 to 5 parts by weight of an organic peroxide. The outer cover layer has a lower Shore D hardness than the inner cover layer.

The polybutadiene (a) is typically synthesized using a rare-earth catalyst.

Preferably, the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of not more than 55, and satisfies the relationship  $\eta \leq 20A - 550$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene and  $\eta$  is the viscosity, in mPa·s, of the second polybutadiene at 25° C. as a 5 wt % solution in toluene. The second polybutadiene in component (b) is typically synthesized using a Group VIII catalyst.

In the multi-piece solid golf ball of the invention, it is generally advantageous for the inner cover layer to have a Shore D hardness of 50 to 80 and the outer cover layer to have a Shore D hardness of 35 to 60.

**DETAILED DESCRIPTION OF THE INVENTION**

The golf ball of the invention includes a solid core made of a rubber composition in which the base rubber is at least partly polybutadiene. It is critical that the base rubber contain as component (a) a specific amount of a polybutadiene in which the cis-1,4 and 1,2 vinyl contents, the viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene, and the relationship between the Mooney viscosity and the polydispersity index Mw/Mn have each been optimized.

That is, the polybutadiene (a) has a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least

US 6,634,961 B2

3

90%, and most preferably at least 95%; and has a 1,2 vinyl content of at most 2%, preferably at most 1.7%, more preferably at most 1.5%, and most preferably at most 1.3%. Outside of the above ranges, the resilience declines.

The polybutadiene (a) must also have a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s. "Viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene" refers herein to the value in mPa·s units obtained by dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene and carrying out measurement with a specified viscometer at 25° C. using a standard solution for the viscometer (JIS Z8809).

The polybutadiene (a) has a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s, preferably not more than 550 mPa·s, more preferably not more than 500 mPa·s, even more preferably not more than 450 mPa·s, and most preferably not more than 400 mPa·s. Too high a viscosity  $\eta$  lowers the workability of the rubber composition. It is recommended that the viscosity  $\eta$  be at least 50 mPa·s, preferably at least 100 mPa·s, more preferably at least 150 mPa·s, and most preferably at least 200 mPa·s. Too low a viscosity  $\eta$  may lower the resilience.

In addition, the polybutadiene (a) must satisfy the relationship:

$$10B+5 \leq A \leq 10B+60,$$

wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene. A is preferably at least 10B+7, more preferably at least 10B+8 and most preferably at least 10B+9, but preferably not more than 10B+55, more preferably not more than 10B+50, and most preferably not more than 10B+45. If A is too low, the resilience declines. On the other hand, if A is too high, the workability of the rubber composition worsens.

It is recommended that the polybutadiene (a) have a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of at least 20, preferably at least 30, more preferably at least 40, and most preferably at least 50, but not more than 80, preferably not more than 70, more preferably not more than 65, and most preferably not more than 60.

The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol  $ML_{1+4}$  (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

It is desirable for the polybutadiene (a) to be synthesized using a rare-earth catalyst. A known rare-earth catalyst may be used for this purpose.

Examples of suitable catalysts include lanthanide series rare-earth compounds, organoaluminum compounds, alumoxane, halogen-bearing compounds, optionally in combination with Lewis bases.

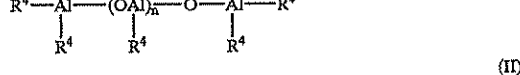
Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals.

Organoaluminum compounds that may be used include those of the formula  $AlR^1R^2R^3$  (wherein  $R^1$ ,  $R^2$  and  $R^3$  are

4

each independently a hydrogen or a hydrocarbon residue of 1 to 8 carbons).

Preferred alumoxanes include compounds of the structures shown in formulas (I) and (II) below. The alumoxane association complexes described in *Fine Chemical* 23, No. 9, 5 (1994), *J. Am. Chem. Soc.* 115, 4971 (1993), and *J. Am. Chem. Soc.* 117, 6465 (1995) are also acceptable.



In the above formulas,  $R^4$  is a hydrocarbon group having 1 to 20 carbon atoms, and n is 2 or a larger integer.

Examples of halogen-bearing compounds that may be used include aluminum halides of the formula  $AlX_nR_{3-n}$  (wherein X is a halogen; R is a hydrocarbon residue of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as  $Me_3SrCl$ ,  $Me_2SrCl_2$ ,  $MeSrHCl_2$  and  $MeSrCl_3$  (wherein "Me" stands for methyl); and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride.

The Lewis base may be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols.

In the practice of the invention, the use of a neodymium catalyst composed in part of a neodymium compound as the lanthanide series rare-earth compound is advantageous because it enables a polybutadiene rubber having a high cis-1,4 content and a low 1,2 vinyl content to be obtained at an excellent polymerization activity. Preferred examples of such rare-earth catalysts include those mentioned in JP-A 11-35633.

The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature in a range of generally -30° C. to +150° C., and preferably 10° C. to 100° C.

It is also possible for the polybutadiene (a) to be obtained by polymerization using the above-described rare-earth catalyst, followed by the reaction of an end group modifier with active end groups on the polymer.

Any known end group modifier may be used. Examples include compounds of types (1) to (6) described below:

- (1) halogenated organometallic compounds, halogenated metallic compounds and organometallic compounds of the general formulas  $R^5_nM'X_{4-n}$ ,  $M'X_4$ ,  $M'X_3$ ,  $R^5_nM'(-R^6-COOR^7)_{4-n}$  or  $R^5_nM'(-R^6-COR^7)_{4-n}$  (wherein  $R^5$  and  $R^6$  are each independently a hydrocarbon group of 1 to 20 carbons;  $R^7$  is a hydrocarbon group of 1 to 20 carbons which may contain a carbonyl or ester moiety as a side chain;  $M'$  is a tin atom, silicon atom, germanium atom or phosphorus atom; X is a halogen atom; and n is an integer from 0 to 3);
- (2) heterocumulene compounds containing on the molecule a  $Y=C=Z$  linkage (wherein Y is a carbon atom, oxygen atom, nitrogen atom or sulfur atom; and Z is an oxygen atom, nitrogen atom or sulfur atom);



US 6,634,961 B2

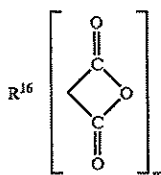
5

- (3) three-membered heterocyclic compounds containing on the molecule the following bonds



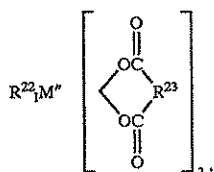
(wherein Y is an oxygen atom, a nitrogen atom or a sulfur atom);

- (4) halogenated isocyano compounds;  
 (5) carboxylic acids, acid halides, ester compounds, carbonate compounds or acid anhydrides of the formulas  $R^8-(COOH)_m$ ,  $R^9(COX)_m$ ,  $R^{10}-(COO-R^{11})_m$ ,  $R^{12}-OCOO-R^{13}$ ,  $R^{14}-(COOCO-R^{15})_m$  or the following formula



(wherein  $R^8$  to  $R^{16}$  are each independently a hydrocarbon group of 1 to 50 carbons; X is a halogen atom; and m is an integer from 1 to 5); and

- (6) carboxylic acid metal salts of the formula  $R^{17}_1M''(OCOR^{18})_{4-1}$ ,  $R^{19}_1M''(OCO-R^{20}-COOR^{21})_{4-1}$  or the following formula



(wherein  $R^{17}$  to  $R^{23}$  are each independently a hydrocarbon group of 1 to 20 carbons,  $M''$  is a tin atom, a silicon atom or a germanium atom; and 1 is an integer from 0 to 3).

Illustrative examples of the end group modifiers of types (1) to (6) above and methods for their reaction are described in, for instance, JP-A 11-35633 and JP-A 7-268132.

In the practice of the invention, component (a) is included in the base rubber in an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, and most preferably at least 35 wt %. The upper limit is 100 wt %, preferably not more than 90 wt %, more preferably not more than 80 wt %, and most preferably not more than 70 wt %.

In addition to component (a), the base rubber may include also a diene rubber (b) insofar as the objects of the invention are attainable. Specific examples of the diene rubbers (b) include polybutadiene rubber, styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDM). Any one or combination of two or more thereof may be used.

The diene rubber (b) is included together with component (a) in the base rubber in an amount of at least 0 wt %, preferably at least 10 wt %, more preferably at least 20 wt %, and most preferably at least 30 wt %, but not more than 80 wt %, preferably not more than 75 wt %, more preferably not more than 70 wt %, and most preferably not more than 65 wt %.

6

In the practice of the invention, it is preferable for component (b) to include a polybutadiene rubber, and especially one for which the cis-1,4 and 1,2 vinyl contents, the Mooney viscosity, and the relationship between the Mooney viscosity and  $\eta$  have each been optimized. The polybutadiene serving as component (b) is referred to as "second polybutadiene" in order to distinguish it from the polybutadiene serving as component (a).

It is recommended that the second polybutadiene in component (b) have a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least 90%, and most preferably at least 95%, and that it have a 1,2 vinyl content of at most 5%, preferably at most 4.5%, more preferably at most 4.0%, and most preferably at most 3.5%.

It is recommended that the second polybutadiene have a Mooney viscosity of at least 10, preferably at least 20, more preferably at least 25, and most preferably at least 30, but not more than 55, preferably not more than 50, and most preferably not more than 45.

In the practice of the invention, it is recommended that the second polybutadiene be one that has been synthesized using a Group VIII catalyst. Exemplary Group VIII catalysts include nickel catalysts and cobalt catalysts.

Examples of suitable nickel catalysts include single-component systems such as nickel-kieselguhr, binary systems such as Raney nickel/titanium tetrachloride, and ternary systems such as nickel compound/organometallic compound/boron trifluoride etherate. Exemplary nickel compounds include reduced nickel on a carrier, Raney nickel, nickel oxide, nickel carboxylate and organonickel complexes. Exemplary organometallic compounds include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum and tri-n-hexylaluminum; alkyl lithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium and 1,4-dilithiobutane; and dialkylzinc compounds such as diethylzinc and dibutylzinc.

Examples of suitable cobalt catalysts include the following composed of cobalt or cobalt compounds: Raney cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyldithiocarbamate, cobalt anilinium nitrite and cobalt dinitrosyl chloride. It is particularly advantageous to use the above in combination with a dialkylaluminum monochloride such as diethylaluminum monochloride or diisobutylaluminum monochloride; a trialkylaluminum such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum or tri-n-hexylaluminum; an alkyl aluminum sesquichloride such as ethylaluminum sesquichloride; or aluminum chloride.

Polymerization using the Group VIII catalysts described above, and especially a nickel or cobalt catalyst, can generally be carried out by a process in which the catalyst is continuously charged into the reactor together with the solvent and butadiene monomer, and the reaction conditions are suitably selected from a temperature range of 5 to 60° C. and a pressure range of atmospheric pressure to 70 plus atmospheres, so as to yield a product having the above-indicated Mooney viscosity.

It is also desirable for the second polybutadiene in component (b) to satisfy the relationship:

$$20A-750 \leq \eta \leq 20A-550$$

wherein  $\eta$  is the viscosity of the second polybutadiene at 25° C. as a 5 wt % solution in toluene and A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene.

US 6,634,961 B2

7

The viscosity  $\eta$  is preferably at least 20A-700, more preferably at least 20A-680, and most preferably at least 20A-650, but preferably not more than 20A-560, more preferably not more than 20A-580, and most preferably not more than 20A-590. The use of a polybutadiene having such an optimized relationship of  $\eta$  and A, that suggests the high linearity of polybutadiene molecules, is effective for conferring better resilience and workability.

The second polybutadiene generally accounts for at least 30 wt %, preferably at least 50 wt %, and most preferably at least 70 wt %, and up to 100 wt %, preferably up to 90 wt %, and most preferably up to 80 wt %, of the diene rubber (b). By including the second polybutadiene within component (b) in the foregoing range, even better extrudability and hence, workability during manufacture can be conferred.

The solid core in the golf balls of the invention is molded from a rubber composition containing as essential components specific amounts of (c) an unsaturated carboxylic acid and/or metal salt thereof, (d) an organosulfur compound, (e) an inorganic filler and (f) an organic peroxide per 100 parts by weight of the base rubber.

Specific examples of unsaturated carboxylic acids that may be used as component (c) include acrylic acid, methacrylic acid, maleic acid and fumaric acid. Acrylic acid and methacrylic acid are especially preferred.

Specific examples of unsaturated carboxylic acid metal salts that may be used as component (c) include the zinc and magnesium salts of unsaturated fatty acids such as zinc methacrylate and zinc acrylate. Zinc acrylate is especially preferred.

The unsaturated carboxylic acid and/or metal salt thereof used as component (c) is included in an amount, per 100 parts by weight of the base rubber, of at least 10 parts by weight, preferably at least 15 parts by weight, and most preferably at least 20 parts by weight, but not more than 60 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much component (c) results in excessive hardness, giving the golf ball a feel upon impact that is difficult for the player to endure. On the other hand, too little component (c) undesirably lowers the resilience.

The organosulfur compound (d) of the rubber composition is essential for imparting good resilience. Exemplary organosulfur compounds include thiophenol, thionaphthol, halogenated thiophenols, and metal salts thereof. Specific examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, and zinc salts thereof, such as the zinc salt of pentachlorothiophenol; and organosulfur compounds having 2 to 4 sulfurs, such as diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides. Diphenyl disulfide and the zinc salt of pentachlorothiophenol are especially preferred.

The organosulfur compound (d) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.2 part by weight, and most preferably at least 0.5 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much organosulfur compound results in an excessively low hardness, whereas too little makes it impossible to enhance the resilience.

Examples of inorganic fillers that may be used as component (e) include zinc oxide, barium sulfate and calcium

8

carbonate. The inorganic filler (e) is included in an amount, per 100 parts by weight of the base rubber, of at least 5 parts by weight, preferably at least 7 parts by weight, more preferably at least 10 parts by weight, and most preferably at least 13 parts by weight, but not more than 80 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much or too little inorganic filler makes it impossible to achieve a golf ball core having an appropriate weight and good rebound characteristics.

The organic peroxide (f) may be a commercial product, suitable examples of which include Percumil D (manufactured by NOF Corporation), Perhexa 3M (manufactured by NOF Corporation) and Luperco 231XL (manufactured by Atochem Co.). If necessary, two or more different organic peroxides may be mixed and used together.

The organic peroxide (f) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.3 part by weight, more preferably at least 0.5 part by weight, and most preferably at least 0.7 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much or too little organic peroxide makes it impossible to achieve a ball having a good feel upon impact and good durability and rebound characteristics.

If necessary, the rubber composition may also include an antioxidant, suitable examples of which include such commercial products as Nocrac NS-6, Nocrac NS-30 (both made by Ouchi Shinko Chemical Industry Co., Ltd.), and Yoshinox 425 (made by Yoshitomi Pharmaceutical Industries, Ltd.). The use of such an antioxidant in an amount, per 100 parts by weight of the base rubber, of at least 0 part by weight, preferably at least 0.05 part by weight, more preferably at least 0.1 part by weight, and most preferably at least 0.2 part by weight, but not more than 3 parts by weight, preferably not more than 2 parts by weight, more preferably not more than 1 part by weight, and most preferably not more than 0.5 part by weight, is desirable for achieving good rebound characteristics and durability.

The solid core of the invention can be produced by vulcanizing and curing the above-described rubber composition using a method like that employed with known rubber compositions for golf balls. For example, vulcanization may be carried out at a temperature of 100 to 200° C. for a period of 10 to 40 minutes.

In the practice of the invention, the solid core has a hardness which is suitably adjusted according to its manner of use in the various golf ball constructions that may be employed and is not subject to any particular limitation. The core may have a cross-sectional hardness profile which is flat from the center to the surface thereof, or which varies from the center to the surface.

It is recommended that the solid core have a deflection, when subjected to a load of 980 N (100 kg), of at least 2.0 mm, preferably at least 2.5 mm, more preferably at least 2.8 mm, and most preferably at least 3.2 mm, but not more than 6.0 mm, preferably not more than 5.5 mm, more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. Too small a deformation may worsen the feel of the ball upon impact and, particularly on long shots such as with a driver in which the ball incurs a large deformation, may subject the ball to an excessive rise in spin, reducing the carry. On the other hand, if the solid core is too soft, the golf ball tends to have a dead feel when hit, an inadequate

US 6,634,961 B2

9

rebound that results in a poor carry, and a poor durability to cracking with repeated impact.

It is recommended that the solid core in the inventive golf ball have a diameter of at least 30.0 mm, preferably at least 32.0 mm, more preferably at least 34.0 mm, and most preferably at least 35.0 mm, but not more than 40.0 mm, preferably not more than 39.5 mm, and most preferably not more than 39.0 mm.

It is also recommended that the solid core have a specific gravity of at least 0.9, preferably at least 1.0, and most preferably at least 1.1, but not more than 1.4, preferably not more than 1.3, and most preferably not more than 1.2.

The golf ball of the invention is a multi-piece solid golf ball having a cover composed of at least two layers which are referred to herein as the "inner cover layer" and the "outer cover layer." Such cover layers can be produced from known cover stock. The cover stocks used to make both cover layers in the inventive golf ball may be composed primarily of a thermoplastic or thermoset polyurethane elastomer, polyester elastomer, ionomer resin, ionomer resin having a relatively high degree of neutralization, polyolefin elastomer or mixture thereof. Any one or mixture of two or more thereof may be used, although the use of a thermoplastic polyurethane elastomer, ionomer resin or ionomer resin having a relatively high degree of neutralization is especially preferred.

Illustrative examples of thermoplastic polyurethane elastomers that may be used for the above purpose include commercial products in which the diisocyanate is an aliphatic or aromatic compound, such as Pandex T7298, Pandex T7295, Pandex T7890, Pandex TR3080, Pandex T8290, Pandex T8295 and Pandex T1188 (all manufactured by DIC Bayer Polymer, Ltd.). Illustrative examples of suitable commercial ionomer resins include Surlyn 6320, Surlyn 8945, Surlyn 9945 and Surlyn 8120 (both products of E. I. du Pont de Nemours and Co., Inc.), and Himilan 1706, Himilan 1605, Himilan 1855, Himilan 1557, Himilan 1601 and Himilan AM7316 (all products of DuPont-Mitsui Polychemicals Co., Ltd.).

Together with the primary material described above, the cover stock may include also, as an optional material, polymers (e.g., thermoplastic elastomers) other than the foregoing. Specific examples of polymers that may be included as optional constituents include polyamide elastomers, styrene block elastomers, hydrogenated polybutadienes and ethylene-vinyl acetate (EVA) copolymers.

The multi-piece solid golf ball of the invention can be manufactured by any suitable known method without particular limitation. In one preferred method, the solid core is placed within a given injection mold, following which a predetermined method is used to successively inject over the core the above-described inner and outer cover layer materials. In another preferred method, each of the cover stocks is formed into a pair of half cups, and the resulting pairs are successively placed over the solid core and compression molded.

In the golf balls of the invention, it is critical that the outer cover layer have a lower Shore D hardness than the inner cover layer.

It is recommended that the inner cover layer have a Shore D hardness of at least 50, preferably at least 51, more preferably at least 52, and most preferably at least 53, but not more than 80, preferably not more than 75, more preferably not more than 70, and most preferably not more than 65.

10

It is recommended that the outer cover layer have a Shore D hardness of at least 35, preferably at least 40, more preferably at least 45, and most preferably at least 48, but not more than 60, preferably not more than 58, more preferably not more than 56, and most preferably not more than 54.

As noted above, in the practice of the invention the outer cover layer must have a lower Shore D hardness than the inner cover layer. It is advantageous for the inner and outer cover layers to have a difference in Shore D hardness of at least 2, preferably at least 5, more preferably at least 7, and most preferably at least 9 Shore D hardness units, but not more than 30, preferably not more than 25, and most preferably not more than 20 Shore D hardness units.

It is recommended that the inner and outer cover layers have a respective thickness of at least 0.7 mm, and preferably at least 1.0 mm, but not more than 3.0 mm, preferably not more than 2.5 mm, even more preferably not more than 2.0 mm, and most preferably not more than 1.6 mm.

The multi-piece solid golf ball of the invention can be manufactured for competitive use by imparting the ball with a diameter and weight which conform with the Rules of Golf; that is, a diameter of at least 42.67 mm and a weight of not more than 45.93 g. It is recommended that the diameter be no more than 44.0 mm, preferably no more than 43.5 mm, and most preferably no more than 43.0 mm; and that the weight be at least 44.5 g, preferably at least 45.0 g, more preferably at least 45.1 g, and most preferably at least 45.2 g.

Multi-piece solid golf balls according to the present invention have a good, soft feel upon impact and an excellent spin performance that enable the ball to travel a greater distance when played.

## EXAMPLES

The following examples and comparative examples are provided to illustrate the invention, and are not intended to limit the scope thereof.

### Examples 1-5 & Comparative Examples 1-4

The core materials shown in Table 2 were formulated in the indicated amounts per 100 parts by weight of polybutadiene material composed of polybutadiene types (1) to (7) below in the proportions shown in Table 1. The resulting core formulations were blended in a kneader or on a roll mill, then molded under applied pressure at 150° C. for 20 minutes to form solid cores having a diameter of about 36.4 mm.

#### Types of Polybutadiene

- (1) BR01, made by JSR Corporation
- (2) BR11, made by JSR Corporation
- (3) UBE101, made by Ube Industries, Ltd.
- (4) HCBN-4, an experimental grade of polybutadiene made by JSR Corporation
- (5) HCBN-2, an experimental grade of polybutadiene made by JSR Corporation
- (6) Experimental grade #9100081 made by Firestone
- (7) Experimental grade #9100069 made by Firestone



US 6,634,961 B2

11

12

TABLE 1

Type	Catalyst	cis-1,4 content, %	1,2 vinyl content, %	Mooney viscosity (A)	Mw/Mn (B)	$\eta$	10B + 5	10B + 60	20A - 550
<u>Polybutadiene</u>									
(1)	Ni	96	2.5	44	4.2	150	47	102	330
(2)	Ni	96	2	44	4.4	270	49	104	330
(3)	Co	95	3	38	4.2	130	47	102	210
(4)	Nd	96	1.1	44	3.5	390	40	95	330
(5)	Nd	96	0.9	40	3.3	280	38	93	250
(6)	Nd	95	1.5	56	2.6	370	31	86	570
(7)	Nd	96	1.3	48	2.5	280	30	85	410

TABLE 2

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
<u>Rubber formulation (pbw)</u>									
(1)						50			
(2)	70	30	50		50	50		50	
(3)				50			50		50
(4)	30								
(5)				50	50		50	50	50
(6)		70							
(7)			50						
<u>Core formulation (pbw)</u>									
Polybutadiene	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.4	1.4	1.4	0.7	0.7	1.4	1.4	1.4	1.4
1,1-Bis(t-butylperoxy)- 3,3,5-trimethylcyclo hexane				0.3	0.3				
Zinc oxide	18	18	15.5	27	26	26	28.5	27	26
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc acrylate	27	27	31	30	32	32	28	30	32
Zinc salt of pentachlorothiophenol	1	1	2	1	1	1	0	1	1

The resulting solid cores were tested as described below to determine their deformation under 980 N (100 kg) loading and their rebound. The results are shown in Table 4.

#### Deformation Under 980 N Loading

Measured as the deflection (mm) of the solid core when subjected to a load of 980 N (100 kg).

#### Rebound

The initial velocity of the solid cores was measured with the same type of initial velocity instrument as used by the official regulating body—the United States Golf Association (USGA). Each rebound value shown in Table 4 is the difference between the initial velocity of the solid core obtained in that particular example and the initial velocity of the solid core obtained in Comparative Example 2.

In each example, the resulting solid core was placed in a given mold and the appropriate resin shown in Table 3 was injection-molded over the core, thereby producing an inner layer-covered core having a diameter of about 39.7 mm. The covered core was then transferred to a given mold, and the appropriate resin shown in Table 3 was injection molded over the covered core, yielding a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g. Trade names appearing in Table 3 are described below.

Himilan: An ionomer resin produced by DuPont-Mitsui Polychemicals Co., Ltd.

Surllyn: An ionomer resin produced by E. I. du Pont de Nemours and Co.

Dynaron: An E-EB-E block copolymer produced by JSR Corporation

Pandex: A polyurethane elastomer produced by Bayer-DIC Polymer, Ltd.

The properties of the resulting golf balls were determined as described below. The results are shown in Table 4.

#### Material Properties

The Shore D hardnesses of the inner cover layer and the outer cover layer were measured with a durometer by the test method described in ASTM D2240.

#### Golf Ball Properties

The carry and total distance were measured when the ball was hit at a head speed (HS) of 50 m/s with a driver (No. 1 Wood) mounted on a swing machine.

#### Feel

The feel of the ball when actually shot with a driver (No. 1 Wood) and putter was rated by five professional and five top-caliber amateur golfers as "Too hard," "Good" or "Too soft." The rating assigned most often to a particular ball was used as that ball's overall rating.



US 6,634,961 B2

13

TABLE 3

	A	B	C	D	E	F	G
Formulation (pbw)							
Himilan 1706	50	70					
Himilan 1605	50						
Himilan 1557						20	
Himilan 1855						30	
Himilan AM7316		12					
Suriya 8945			35				
Suriya 9945			35				
Suriya 8120				100			50
Dynaron 6100P			30				15
Pandex T8290					50		
Pandex T8295					50	100	
Behenic acid		16					
Magnesium oxide		2					
Titanium dioxide	4	2	4	4	2.7	2.7	4

14

Japanese patent application Ser. No. 2001-163238 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising

100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, being synthesized using a rare-earth catalyst and satisfying the relationship:  $10B + 5 \leq A \leq 10B + 60$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio  $M_w/M_n$  between the weight-average molecular weight  $M_w$  and the number-average molecular weight  $M_n$  of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a),

TABLE 4

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
<b>Core properties</b>									
Deflection (mm) under 980 N load	3.8	3.8	3.5	3.5	3.3	3.3	3.5	3.5	3.3
Specific gravity	1.15	1.15	1.15	1.21	1.21	1.21	1.21	1.21	1.21
Rebound (m/s)	+0.9	+0.9	+1.1	+0.7	+0.8	+0.3	0	+0.5	+0.5
<b>Inner cover layer</b>									
Type	A	B	C	A	B	B	A	D	D
Shore D hardness	63	60	56	63	60	60	63	45	45
Specific gravity	0.98	0.97	0.97	0.98	0.97	0.97	0.98	0.98	0.98
Thickness (mm)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
<b>Outer cover layer</b>									
Type	E	F	F	G	G	G	G	G	A
Shore D hardness	47	51	51	53	53	53	53	53	63
Specific gravity	1.18	1.18	1.18	0.98	0.98	0.98	0.98	0.98	0.98
Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
<b>Golf ball properties</b>									
When hit with No. 1 Wood at HS of 50 m/s									
Carry (m)	227.0	226.9	226.7	226.9	226.7	223.8	222.2	217.7	220.8
Total distance (m)	258.5	258.8	258.3	258.3	258.0	255.0	253.4	248.3	252.8
Spin rate (rpm)	3205	3153	3241	3125	3180	3182	3121	3305	3177
Feel on impact	good	good	good	good	good	good	good	too soft	good
Spin rate on approach shot (sand wedge; HS 20 m/s)	6323	6251	6226	6118	6111	6107	6113	6186	4308
Feel of ball	good	good	good	good	good	good	good	too soft	too hard

US 6,634,961 B2

15

- (c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both,
  - (d) 0.1 to 5 parts by weight of an organosulfur compound,
  - (e) 5 to 80 parts by weight of an inorganic filler,
  - (f) 0.1 to 5 parts by weight of an organic peroxide;
- the inner cover layer has a Shore D hardness of 50 to 80; the outer cover layer has a Shore D hardness of 35 to 60; and

the outer cover layer has a lower Shore D hardness than the inner cover layer.

- 2. The golf ball of claim 1, wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of not more than 55, and satisfies the relationship:

$$\eta \leq 20A - 550,$$

wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene and  $\eta$  is the viscosity of the second polybutadiene, in mPa·s, at 25° C. as a 5 wt % solution in toluene.

16

- 3. The golf ball of claim 1 wherein said polybutadiene (a) is synthesized by using neodymium catalyst.

- 4. The golf ball of claim 1 wherein said polybutadiene (a) has a Mooney viscosity ( $ML_{1+4}$ , 100° C.) of 40 to 60.

- 5. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 5 units.

- 6. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 7 units.

- 7. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 9 units.

- 8. The golf ball of claim 1, wherein said ball is three-piece construction consisting of a solid core, an inner cover layer and an outer cover layer.

- 9. The golf ball of claim 2, wherein the second polybutadiene in component (b) is synthesized using a Group VIII catalyst.

\* \* \* \* \*

US006634961B2

(12) **United States Patent**  
**Higuchi et al.**

(10) **Patent No.:** **US 6,634,961 B2**  
(45) **Date of Patent:** **\*Oct. 21, 2003**

(54) **MULTI-PIECE SOLID GOLF BALL**

(75) Inventors: **Hiroshi Higuchi**, Chichibu (JP);  
**Atsushi Nanba**, Chichibu (JP)

(73) Assignee: **Bridgestone Sports Co., Ltd.**, Tokyo  
(JP)

(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-  
claimer.

(21) Appl. No.: **10/156,950**

(22) Filed: **May 30, 2002**

(65) **Prior Publication Data**

US 2003/0017888 A1 Jan. 23, 2003

(30) **Foreign Application Priority Data**

May 30, 2001 (JP) ..... 2001-163238

(51) **Int. Cl.<sup>7</sup>** ..... **A63B 37/06**

(52) **U.S. Cl.** ..... **473/357; 524/432**

(58) **Field of Search** ..... **473/357, 356,**  
**473/359, 372, 374, 371, 373; 524/194,**  
**908, 432, 526, 534**

(56) **References Cited**

#### U.S. PATENT DOCUMENTS

4,683,257 A \* 7/1987 Kakiuchi et al. .... 473/372  
4,929,678 A \* 5/1990 Hamada et al. .... 525/193  
4,955,613 A \* 9/1990 Gendreau et al. .... 260/998.14  
5,252,652 A \* 10/1993 Egashira et al. .... 473/372

5,733,205 A \* 3/1998 Higuchi et al. .... 473/373  
6,045,460 A \* 4/2000 Hayashi et al. .... 473/376  
6,194,505 B1 \* 2/2001 Sone et al. .... 473/371  
6,315,679 B1 \* 11/2001 Sano ..... 473/357

#### FOREIGN PATENT DOCUMENTS

EP 0 920 886 A2 6/1999  
GB 2 324 740 A 11/1998

#### OTHER PUBLICATIONS

M. R. Farrally, A. J. Cochran, "Science and Golf III", 1999,  
Human Kinetics, pp. 410, 412, 413.\*  
British Search Report, Oct. 17, 2002.

\* cited by examiner

*Primary Examiner*—Paul T. Sewell

*Assistant Examiner*—Tom P. Duong

(74) *Attorney, Agent, or Firm*—Sughrue Mion, PLLC

(57) **ABSTRACT**

In a multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, the solid core is molded from a rubber composition comprising a base rubber composed of (a) 20–100 wt % of a polybutadiene having a high cis-1,4 content, a minimal 1,2 vinyl content and a viscosity  $\eta$  of up to 600 mPa·s at 25° C as a 5 wt % toluene solution, and satisfying a certain relationship between Mooney viscosity and polydispersity index in combination with (b) 0–80 wt % of another diene rubber, (c) an unsaturated carboxylic acid, (d) an organosulfur compound, (e) an inorganic filler, and (f) an organic peroxide; and the outer cover layer has a lower Shore D hardness than the inner cover layer. This combination of features gives the ball a good, soft feel upon impact and an excellent spin performance that provides increased distance.

**9 Claims, No Drawings**

US 6,634,961 B2

1

## MULTI-PIECE SOLID GOLF BALL

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

The present invention relates to a multi-piece solid golf ball which has been imparted with a good, soft feel upon impact and an excellent spin performance that makes it possible to achieve an increased distance.

## 2. Prior Art

Various improvements are being made in formulating the polybutadiene used as the base rubber in golf balls so as to confer the balls with outstanding rebound characteristics.

For example, JP-A 62-89750 describes rubber compositions for use as the base rubber in solid golf balls, which compositions are arrived at by blending a polybutadiene having a Mooney viscosity of 70 to 100 and synthesized using a nickel or cobalt catalyst with another polybutadiene having a Mooney viscosity of 30 to 90 and synthesized using a lanthanide catalyst or polybutadiene having a Mooney viscosity of 20 to 50 and synthesized using a nickel or cobalt catalyst.

However, further improvements in the materials are required in the above art to achieve golf balls endowed with a good, soft feel upon impact and an excellent spin performance that helps increase the distance the ball travels when played.

JP-A 2-268778 describes golf balls molded using a blend composed of a polybutadiene having a Mooney viscosity of less than 50 and synthesized using a Group VIII catalyst in combination with a polybutadiene having a Mooney viscosity of less than 50 and synthesized with a lanthanide catalyst. However, golf balls with a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball cannot be obtained in this way.

The existing art also teaches multi-piece solid golf balls in which an intermediate layer is molded of a low-Mooney viscosity polybutadiene (JP-A 11-70187), solid golf balls molded from rubber compositions comprising a polybutadiene having a Mooney viscosity of 50 to 69 and synthesized using a nickel or cobalt catalyst in combination with a polybutadiene having a Mooney viscosity of 20 to 90 and synthesized using a lanthanide catalyst (JP-A 11-319148), solid golf balls molded from compositions based on a rubber having a 1,2 vinyl content of at most 2.0% and a weight-average molecular weight to number-average molecular weight ratio Mw/Mn of not more than 3.5 (JP-A 11-164912), golf balls molded from rubber compositions containing a high Mooney viscosity polybutadiene (JP-A 63-275356), and golf balls molded from rubber compositions comprising polybutadiene having a high number-average molecular weight in admixture with polybutadiene having a low number-average molecular weight (JP-A 3-151985). However, none of these prior-art golf balls truly have a good, soft feel upon impact and an excellent spin performance that helps increase the distance traveled by the ball.

Golf balls having a cover composed of a relatively hard inner layer and a relatively soft outer layer have already been disclosed in JP-A 6-218078, JP-A 6-343718, JP-A 7-24085, JP-A 9-239068, JP-A 10-151226, JP-A 10-201880, JP-A 11-104273, JP-A 11-104271, and Japanese Patent Applications No. 2000-274807 and 2000-274843. However, further improvements in distance are desired for the golf balls described in all of these specifications.

## SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide multi-piece solid golf balls which are endowed with a good,

2

soft feel when hit with a golf club and an excellent spin performance that helps increase the distance traveled by the ball when played.

The inventor has discovered that golf balls having a solid core, an inner cover layer over the cover, and an outer cover layer over the inner cover layer, wherein the solid core is made of a rubber composition formulated from a particular type of base rubber combined in specific proportions with certain other materials, and the outer cover layer is softer than the inner cover layer, exhibit a good synergy from optimization of the solid core materials and an appropriate distribution of hardness between the inner and outer cover layers. Multi-piece solid golf balls thus constituted have a good, soft feel when hit with a golf club and an excellent spin performance that enables the ball to travel further when played.

Accordingly, the invention provides a multi-piece solid golf ball having a solid core, an inner cover layer enclosing the core, and an outer cover layer enclosing the inner cover layer. The solid core is molded from a rubber composition comprising 100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, and satisfying the relationship:  $10B + 5 \leq A \leq 10B + 60$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a). The rubber composition includes also (c) 10 to 60 parts by weight of an unsaturated carboxylic acid and/or a metal salt thereof, (d) 0.1 to 5 parts by weight of an organosulfur compound, (e) 5 to 80 parts by weight of an inorganic filler, and (f) 0.1 to 5 parts by weight of an organic peroxide. The outer cover layer has a lower Shore D hardness than the inner cover layer.

The polybutadiene (a) is typically synthesized using a rare-earth catalyst.

Preferably, the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of not more than 55, and satisfies the relationship  $\eta \leq 20A - 550$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene and  $\eta$  is the viscosity, in mPa·s, of the second polybutadiene at 25° C. as a 5 wt % solution in toluene. The second polybutadiene in component (b) is typically synthesized using a Group VIII catalyst.

In the multi-piece solid golf ball of the invention, it is generally advantageous for the inner cover layer to have a Shore D hardness of 50 to 80 and the outer cover layer to have a Shore D hardness of 35 to 60.

## DETAILED DESCRIPTION OF THE INVENTION

The golf ball of the invention includes a solid core made of a rubber composition in which the base rubber is at least partly polybutadiene. It is critical that the base rubber contain as component (a) a specific amount of a polybutadiene in which the cis-1,4 and 1,2 vinyl contents, the viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene, and the relationship between the Mooney viscosity and the polydispersity index Mw/Mn have each been optimized.

That is, the polybutadiene (a) has a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least



US 6,634,961 B2

3

90%, and most preferably at least 95%; and has a 1,2 vinyl content of at most 2%, preferably at most 1.7%, more preferably at most 1.5%, and most preferably at most 1.3%. Outside of the above ranges, the resilience declines.

The polybutadiene (a) must also have a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s. "Viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene" refers herein to the value in mPa·s units obtained by dissolving 2.28 g of the polybutadiene to be measured in 50 ml of toluene and carrying out measurement with a specified viscometer at 25° C. using a standard solution for the viscometer (JIS Z8809).

The polybutadiene (a) has a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of not more than 600 mPa·s, preferably not more than 550 mPa·s, more preferably not more than 500 mPa·s, even more preferably not more than 450 mPa·s, and most preferably not more than 400 mPa·s. Too high a viscosity  $\eta$  lowers the workability of the rubber composition. It is recommended that the viscosity  $\eta$  be at least 50 mPa·s, preferably at least 100 mPa·s, more preferably at least 150 mPa·s, and most preferably at least 200 mPa·s. Too low a viscosity  $\eta$  may lower the resilience.

In addition, the polybutadiene (a) must satisfy the relationship:

$$10B+5 \leq A \leq 10B+60,$$

wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene. A is preferably at least 10B+7, more preferably at least 10B+8 and most preferably at least 10B+9, but preferably not more than 10B+55, more preferably not more than 10B+50, and most preferably not more than 10B+45. If A is too low, the resilience declines. On the other hand, if A is too high, the workability of the rubber composition worsens.

It is recommended that the polybutadiene (a) have a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of at least 20, preferably at least 30, more preferably at least 40, and most preferably at least 50, but not more than 80, preferably not more than 70, more preferably not more than 65, and most preferably not more than 60.

The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol  $ML_{1+4}$  (100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

It is desirable for the polybutadiene (a) to be synthesized using a rare-earth catalyst. A known rare-earth catalyst may be used for this purpose.

Examples of suitable catalysts include lanthanide series rare-earth compounds, organoaluminum compounds, alumoxane, halogen-bearing compounds, optionally in combination with Lewis bases.

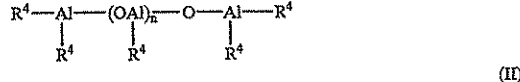
Examples of suitable lanthanide series rare-earth compounds include halides, carboxylates, alcoholates, thioalcoholates and amides of atomic number 57 to 71 metals.

Organoaluminum compounds that may be used include those of the formula  $AlR^1R^2R^3$  (wherein  $R^1$ ,  $R^2$  and  $R^3$  are

4

each independently a hydrogen or a hydrocarbon residue of 1 to 8 carbons).

Preferred alumoxanes include compounds of the structures shown in formulas (I) and (II) below. The alumoxane association complexes described in *Fine Chemical* 23, No. 9, 5 (1994), *J. Am. Chem. Soc.* 115, 4971 (1993), and *J. Am. Chem. Soc.* 117, 6465 (1995) are also acceptable.



In the above formulas,  $R^4$  is a hydrocarbon group having 1 to 20 carbon atoms, and n is 2 or a larger integer.

Examples of halogen-bearing compounds that may be used include aluminum halides of the formula  $AlX_nR_{3-n}$  (wherein X is a halogen; R is a hydrocarbon residue of 1 to 20 carbons, such as an alkyl, aryl or aralkyl; and n is 1, 1.5, 2 or 3); strontium halides such as  $Me_2SrCl$ ,  $Me_2SrCl_2$ ,  $MeSrHCl_2$  and  $MeSrCl_3$  (wherein "Me" stands for methyl); and other metal halides such as silicon tetrachloride, tin tetrachloride and titanium tetrachloride.

The Lewis base may be used to form a complex with the lanthanide series rare-earth compound. Illustrative examples include acetylacetone and ketone alcohols.

In the practice of the invention, the use of a neodymium catalyst composed in part of a neodymium compound as the lanthanide series rare-earth compound is advantageous because it enables a polybutadiene rubber having a high cis-1,4 content and a low 1,2 vinyl content to be obtained at an excellent polymerization activity. Preferred examples of such rare-earth catalysts include those mentioned in JP-A 11-35633.

The polymerization of butadiene in the presence of a rare-earth catalyst may be carried out by bulk polymerization or vapor phase polymerization, either with or without the use of solvent, and at a polymerization temperature in a range of generally -30° C. to +150° C., and preferably 10° C. to 100° C.

It is also possible for the polybutadiene (a) to be obtained by polymerization using the above-described rare-earth catalyst, followed by the reaction of an end group modifier with active end groups on the polymer.

Any known end group modifier may be used. Examples include compounds of types (1) to (6) described below:

(1) halogenated organometallic compounds, halogenated metallic compounds and organometallic compounds of the general formulas  $R^5_nM^5X_{4-n}$ ,  $M^5X_4$ ,  $M^5X_3$ ,  $R^5_nM^5$  ( $-R^6-COOR^7$ ) $_{4-n}$  or  $R^5_nM^5(-R^6-COR^7)$  $_{4-n}$  (wherein  $R^5$  and  $R^6$  are each independently a hydrocarbon group of 1 to 20 carbons;  $R^7$  is a hydrocarbon group of 1 to 20 carbons which may contain a carbonyl or ester moiety as a side chain;  $M^5$  is a tin atom, silicon atom, germanium atom or phosphorus atom; X is a halogen atom; and n is an integer from 0 to 3);

(2) heterocumulene compounds containing on the molecule a  $Y=C=Z$  linkage (wherein Y is a carbon atom, oxygen atom, nitrogen atom or sulfur atom; and Z is an oxygen atom, nitrogen atom or sulfur atom);

US 6,634,961 B2

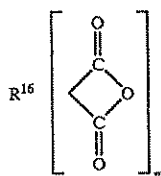
5

- (3) three-membered heterocyclic compounds containing on the molecule the following bonds



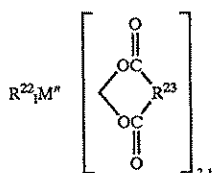
(wherein Y is an oxygen atom, a nitrogen atom or a sulfur atom);

- (4) halogenated isocyanate compounds;  
 (5) carboxylic acids, acid halides, ester compounds, carbonate compounds or acid anhydrides of the formulas  $R^8-(COOH)_m$ ,  $R^9(COX)_m$ ,  $R^{10}-(COO-R^{11})_m$ ,  $R^{12}-OCOO-R^{13}$ ,  $R^{14}-(COOCO-R^{15})_m$  or the following formula



(wherein  $R^8$  to  $R^{16}$  are each independently a hydrocarbon group of 1 to 50 carbons; X is a halogen atom; and m is an integer from 1 to 5); and

- (6) carboxylic acid metal salts of the formula  $R^{17}_1M''(OCOR^{18})_{4-1}$ ,  $R^{19}_1M''(OCO-R^{20}-COOR^{21})_{4-1}$  or the following formula



(wherein  $R^{17}$  to  $R^{23}$  are each independently a hydrocarbon group of 1 to 20 carbons,  $M''$  is a tin atom, a silicon atom or a germanium atom; and 1 is an integer from 0 to 3).

Illustrative examples of the end group modifiers of types (1) to (6) above and methods for their reaction are described in, for instance, JP-A 11-35633 and JP-A 7-268132.

In the practice of the invention, component (a) is included in the base rubber in an amount of at least 20 wt %, preferably at least 25 wt %, more preferably at least 30 wt %, and most preferably at least 35 wt %. The upper limit is 100 wt %, preferably not more than 90 wt %, more preferably not more than 80 wt %, and most preferably not more than 70 wt %.

In addition to component (a), the base rubber may include also a diene rubber (b) insofar as the objects of the invention are attainable. Specific examples of the diene rubbers (b) include polybutadiene rubber, styrene-butadiene rubber (SBR), natural rubber, polyisoprene rubber, and ethylene-propylene-diene rubber (EPDM). Any one or combination of two or more thereof may be used.

The diene rubber (b) is included together with component (a) in the base rubber in an amount of at least 0 wt %, preferably at least 10 wt %, more preferably at least 20 wt %, and most preferably at least 30 wt %, but not more than 80 wt %, preferably not more than 75 wt %, more preferably not more than 70 wt %, and most preferably not more than 65 wt %.

6

In the practice of the invention, it is preferable for component (b) to include a polybutadiene rubber, and especially one for which the cis-1,4 and 1,2 vinyl contents, the Mooney viscosity, and the relationship between the Mooney viscosity and  $\eta$  have each been optimized. The polybutadiene serving as component (b) is referred to as "second polybutadiene" in order to distinguish it from the polybutadiene serving as component (a).

It is recommended that the second polybutadiene in component (b) have a cis-1,4 content of at least 60%, preferably at least 80%, more preferably at least 90%, and most preferably at least 95%, and that it have a 1,2 vinyl content of at most 5%, preferably at most 4.5%, more preferably at most 4.0%, and most preferably at most 3.5%.

It is recommended that the second polybutadiene have a Mooney viscosity of at least 10, preferably at least 20, more preferably at least 25, and most preferably at least 30, but not more than 55, preferably not more than 50, and most preferably not more than 45.

In the practice of the invention, it is recommended that the second polybutadiene be one that has been synthesized using a Group VIII catalyst. Exemplary Group VIII catalysts include nickel catalysts and cobalt catalysts.

Examples of suitable nickel catalysts include single-component systems such as nickel-kieselguhr, binary systems such as Raney nickel/titanium tetrachloride, and ternary systems such as nickel compound/organometallic compound/boron trifluoride etherate. Exemplary nickel compounds include reduced nickel on a carrier, Raney nickel, nickel oxide, nickel carboxylate and organonickel complexes. Exemplary organometallic compounds include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum and tri-n-hexylaluminum; alkyl lithium compounds such as n-butyllithium, sec-butyllithium, tert-butyllithium and 1,4-dilithiobutane; and dialkylzinc compounds such as diethylzinc and dibutylzinc.

Examples of suitable cobalt catalysts include the following composed of cobalt or cobalt compounds: Raney cobalt, cobalt chloride, cobalt bromide, cobalt iodide, cobalt oxide, cobalt sulfate, cobalt carbonate, cobalt phosphate, cobalt phthalate, cobalt carbonyl, cobalt acetylacetonate, cobalt diethyldithiocarbamate, cobalt anilinium nitrite and cobalt dinitrosyl chloride. It is particularly advantageous to use the above in combination with a dialkylaluminum monochloride such as diethylaluminum monochloride or diisobutylaluminum monochloride; a trialkylaluminum such as triethylaluminum, tri-n-propylaluminum, triisobutylaluminum or tri-n-hexylaluminum; an alkyl aluminum sesquichloride such as ethylaluminum sesquichloride; or aluminum chloride.

Polymerization using the Group VIII catalysts described above, and especially a nickel or cobalt catalyst, can generally be carried out by a process in which the catalyst is continuously charged into the reactor together with the solvent and butadiene monomer, and the reaction conditions are suitably selected from a temperature range of 5 to 60° C. and a pressure range of atmospheric pressure to 70 plus atmospheres, so as to yield a product having the above-indicated Mooney viscosity.

It is also desirable for the second polybutadiene in component (b) to satisfy the relationship:

$$20A-750 \leq \eta \leq 20A-550$$

wherein  $\eta$  is the viscosity of the second polybutadiene at 25° C. as a 5 wt % solution in toluene and A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene.

US 6,634,961 B2

7

The viscosity  $\eta$  is preferably at least 20A-700, more preferably at least 20A-680, and most preferably at least 20A-650, but preferably not more than 20A-560, more preferably not more than 20A-580, and most preferably not more than 20A-590. The use of a polybutadiene having such an optimized relationship of  $\eta$  and A, that suggests the high linearity of polybutadiene molecules, is effective for conferring better resilience and workability.

The second polybutadiene generally accounts for at least 30 wt %, preferably at least 50 wt %, and most preferably at least 70 wt %, and up to 100 wt %, preferably up to 90 wt %, and most preferably up to 80 wt %, of the diene rubber (b). By including the second polybutadiene within component (b) in the foregoing range, even better extrudability and hence, workability during manufacture can be conferred.

The solid core in the golf balls of the invention is molded from a rubber composition containing as essential components specific amounts of (c) an unsaturated carboxylic acid and/or metal salt thereof, (d) an organosulfur compound, (e) an inorganic filler and (f) an organic peroxide per 100 parts by weight of the base rubber.

Specific examples of unsaturated carboxylic acids that may be used as component (c) include acrylic acid, methacrylic acid, maleic acid and fumaric acid. Acrylic acid and methacrylic acid are especially preferred.

Specific examples of unsaturated carboxylic acid metal salts that may be used as component (c) include the zinc and magnesium salts of unsaturated fatty acids such as zinc methacrylate and zinc acrylate. Zinc acrylate is especially preferred.

The unsaturated carboxylic acid and/or metal salt thereof used as component (c) is included in an amount, per 100 parts by weight of the base rubber, of at least 10 parts by weight, preferably at least 15 parts by weight, and most preferably at least 20 parts by weight, but not more than 60 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much component (c) results in excessive hardness, giving the golf ball a feel upon impact that is difficult for the player to endure. On the other hand, too little component (c) undesirably lowers the resilience.

The organosulfur compound (d) of the rubber composition is essential for imparting good resilience. Exemplary organosulfur compounds include thiophenol, thionaphthol, halogenated thiophenols, and metal salts thereof. Specific examples include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol, and zinc salts thereof, such as the zinc salt of pentachlorothiophenol; and organosulfur compounds having 2 to 4 sulfurs, such as diphenylpolysulfides, dibenzylpolysulfides, dibenzoylpolysulfides, dibenzothiazoylpolysulfides and dithiobenzoylpolysulfides. Diphenyl disulfide and the zinc salt of pentachlorothiophenol are especially preferred.

The organosulfur compound (d) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.2 part by weight, and most preferably at least 0.5 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much organosulfur compound results in an excessively low hardness, whereas too little makes it impossible to enhance the resilience.

Examples of inorganic fillers that may be used as component (e) include zinc oxide, barium sulfate and calcium

8

carbonate. The inorganic filler (e) is included in an amount, per 100 parts by weight of the base rubber, of at least 5 parts by weight, preferably at least 7 parts by weight, more preferably at least 10 parts by weight, and most preferably at least 13 parts by weight, but not more than 80 parts by weight, preferably not more than 50 parts by weight, more preferably not more than 45 parts by weight, and most preferably not more than 40 parts by weight. Too much or too little inorganic filler makes it impossible to achieve a golf ball core having an appropriate weight and good rebound characteristics.

The organic peroxide (f) may be a commercial product, suitable examples of which include Percumil D (manufactured by NOF Corporation), Perhexa 3M (manufactured by NOF Corporation) and Luperco 231XL (manufactured by Atochem Co.). If necessary, two or more different organic peroxides may be mixed and used together.

The organic peroxide (f) is included in an amount, per 100 parts by weight of the base rubber, of at least 0.1 part by weight, preferably at least 0.3 part by weight, more preferably at least 0.5 part by weight, and most preferably at least 0.7 part by weight, but not more than 5 parts by weight, preferably not more than 4 parts by weight, more preferably not more than 3 parts by weight, and most preferably not more than 2 parts by weight. Too much or too little organic peroxide makes it impossible to achieve a ball having a good feel upon impact and good durability and rebound characteristics.

If necessary, the rubber composition may also include an antioxidant, suitable examples of which include such commercial products as Nocrac NS-6, Nocrac NS-30 (both made by Ouchi Shinko Chemical Industry Co., Ltd.), and Yoshinox 425 (made by Yoshitomi Pharmaceutical Industries, Ltd.). The use of such an antioxidant in an amount, per 100 parts by weight of the base rubber, of at least 0 part by weight, preferably at least 0.05 part by weight, more preferably at least 0.1 part by weight, and most preferably at least 0.2 part by weight, but not more than 3 parts by weight, preferably not more than 2 parts by weight, more preferably not more than 1 part by weight, and most preferably not more than 0.5 part by weight, is desirable for achieving good rebound characteristics and durability.

The solid core of the invention can be produced by vulcanizing and curing the above-described rubber composition using a method like that employed with known rubber compositions for golf balls. For example, vulcanization may be carried out at a temperature of 100 to 200° C. for a period of 10 to 40 minutes.

In the practice of the invention, the solid core has a hardness which is suitably adjusted according to its manner of use in the various golf ball constructions that may be employed and is not subject to any particular limitation. The core may have a cross-sectional hardness profile which is flat from the center to the surface thereof, or which varies from the center to the surface.

It is recommended that the solid core have a deflection, when subjected to a load of 980 N (100 kg), of at least 2.0 mm, preferably at least 2.5 mm, more preferably at least 2.8 mm, and most preferably at least 3.2 mm, but not more than 6.0 mm, preferably not more than 5.5 mm, more preferably not more than 5.0 mm, and most preferably not more than 4.5 mm. Too small a deformation may worsen the feel of the ball upon impact and, particularly on long shots such as with a driver in which the ball incurs a large deformation, may subject the ball to an excessive rise in spin, reducing the carry. On the other hand, if the solid core is too soft, the golf ball tends to have a dead feel when hit, an inadequate



US 6,634,961 B2

9

rebound that results in a poor carry, and a poor durability to cracking with repeated impact.

It is recommended that the solid core in the inventive golf ball have a diameter of at least 30.0 mm, preferably at least 32.0 mm, more preferably at least 34.0 mm, and most preferably at least 35.0 mm, but not more than 40.0 mm, preferably not more than 39.5 mm, and most preferably not more than 39.0 mm.

It is also recommended that the solid core have a specific gravity of at least 0.9, preferably at least 1.0, and most preferably at least 1.1, but not more than 1.4, preferably not more than 1.3, and most preferably not more than 1.2.

The golf ball of the invention is a multi-piece solid golf ball having a cover composed of at least two layers which are referred to herein as the "inner cover layer" and the "outer cover layer." Such cover layers can be produced from known cover stock. The cover stocks used to make both cover layers in the inventive golf ball may be composed primarily of a thermoplastic or thermoset polyurethane elastomer, polyester elastomer, ionomer resin, ionomer resin having a relatively high degree of neutralization, polyolefin elastomer or mixture thereof. Any one or mixture of two or more thereof may be used, although the use of a thermoplastic polyurethane elastomer, ionomer resin or ionomer resin having a relatively high degree of neutralization is especially preferred.

Illustrative examples of thermoplastic polyurethane elastomers that may be used for the above purpose include commercial products in which the diisocyanate is an aliphatic or aromatic compound, such as Pandex T7298, Pandex T7295, Pandex T7890, Pandex TR3080, Pandex T8290, Pandex T8295 and Pandex T1188 (all manufactured by DIC Bayer Polymer, Ltd.). Illustrative examples of suitable commercial ionomer resins include Surlyn 6320, Surlyn 8945, Surlyn 9945 and Surlyn 8120 (both products of E. I. du Pont de Nemours and Co., Inc.), and Himilan 1706, Himilan 1605, Himilan 1855, Himilan 1557, Himilan 1601 and Himilan AM7316 (all products of DuPont-Mitsui Polychemicals Co., Ltd.).

Together with the primary material described above, the cover stock may include also, as an optional material, polymers (e.g., thermoplastic elastomers) other than the foregoing. Specific examples of polymers that may be included as optional constituents include polyamide elastomers, styrene block elastomers, hydrogenated polybutadienes and ethylene-vinyl acetate (EVA) copolymers.

The multi-piece solid golf ball of the invention can be manufactured by any suitable known method without particular limitation. In one preferred method, the solid core is placed within a given injection mold, following which a predetermined method is used to successively inject over the core the above-described inner and outer cover layer materials. In another preferred method, each of the cover stocks is formed into a pair of half cups, and the resulting pairs are successively placed over the solid core and compression molded.

In the golf balls of the invention, it is critical that the outer cover layer have a lower Shore D hardness than the inner cover layer.

It is recommended that the inner cover layer have a Shore D hardness of at least 50, preferably at least 51, more preferably at least 52, and most preferably at least 53, but not more than 80, preferably not more than 75, more preferably not more than 70, and most preferably not more than 65.

10

It is recommended that the outer cover layer have a Shore D hardness of at least 35, preferably at least 40, more preferably at least 45, and most preferably at least 48, but not more than 60, preferably not more than 58, more preferably not more than 56, and most preferably not more than 54.

As noted above, in the practice of the invention the outer cover layer must have a lower Shore D hardness than the inner cover layer. It is advantageous for the inner and outer cover layers to have a difference in Shore D hardness of at least 2, preferably at least 5, more preferably at least 7, and most preferably at least 9 Shore D hardness units, but not more than 30, preferably not more than 25, and most preferably not more than 20 Shore D hardness units.

It is recommended that the inner and outer cover layers have a respective thickness of at least 0.7 mm, and preferably at least 1.0 mm, but not more than 3.0 mm, preferably not more than 2.5 mm, even more preferably not more than 2.0 mm, and most preferably not more than 1.6 mm.

The multi-piece solid golf ball of the invention can be manufactured for competitive use by imparting the ball with a diameter and weight which conform with the Rules of Golf; that is, a diameter of at least 42.67 mm and a weight of not more than 45.93 g. It is recommended that the diameter be no more than 44.0 mm, preferably no more than 43.5 mm, and most preferably no more than 43.0 mm; and that the weight be at least 44.5 g, preferably at least 45.0 g, more preferably at least 45.1 g, and most preferably at least 45.2 g.

Multi-piece solid golf balls according to the present invention have a good, soft feel upon impact and an excellent spin performance that enable the ball to travel a greater distance when played.

## EXAMPLES

The following examples and comparative examples are provided to illustrate the invention, and are not intended to limit the scope thereof.

### Examples 1-5 & Comparative Examples 1-4

The core materials shown in Table 2 were formulated in the indicated amounts per 100 parts by weight of polybutadiene material composed of polybutadiene types (1) to (7) below in the proportions shown in Table 1. The resulting core formulations were blended in a kneader or on a roll mill, then molded under applied pressure at 150° C. for 20 minutes to form solid cores having a diameter of about 36.4 mm.

#### Types of Polybutadiene

- (1) BR01, made by JSR Corporation
- (2) BR11, made by JSR Corporation
- (3) UBE101, made by Ube Industries, Ltd.
- (4) HCBN-4, an experimental grade of polybutadiene made by JSR Corporation
- (5) HCBN-2, an experimental grade of polybutadiene made by JSR Corporation
- (6) Experimental grade #9100081 made by Firestone
- (7) Experimental grade #9100069 made by Firestone



US 6,634,961 B2

11

12

TABLE 1

Type	Catalyst	cis-1,4 content, %	1,2 vinyl content, %	Mooney viscosity (A)	Mw/Mn (B)	$\eta$	10B + 5	10B + 60	20A - 550
<u>Polybutadiene</u>									
(1)	Ni	96	2.5	44	4.2	150	47	102	330
(2)	Ni	96	2	44	4.4	270	49	104	330
(3)	Co	95	3	38	4.2	130	47	102	210
(4)	Nd	96	1.1	44	3.5	390	40	95	330
(5)	Nd	96	0.9	40	3.3	280	38	93	250
(6)	Nd	95	1.5	56	2.6	370	31	86	570
(7)	Nd	96	1.3	48	2.5	280	30	85	410

TABLE 2

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
<u>Rubber formulation (pbw)</u>									
(1)						50			
(2)	70	30	50		50	50		50	
(3)				50			50		50
(4)	30								
(5)				50	50		50	50	50
(6)		70							
(7)			50						
<u>Core formulation (pbw)</u>									
Polybutadiene	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.4	1.4	1.4	0.7	0.7	1.4	1.4	1.4	1.4
1,1-Bis(t-butylperoxy)- 3,3,5-trimethylcyclo hexane				0.3	0.3				
Zinc oxide	18	18	15.5	27	26	26	28.5	27	26
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zinc acrylate	27	27	31	30	32	32	28	30	32
Zinc salt of pentachlorothiophenol	1	1	2	1	1	1	0	1	1

The resulting solid cores were tested as described below to determine their deformation under 980 N (100 kg) loading and their rebound. The results are shown in Table 4.

#### Deformation Under 980 N Loading

Measured as the deflection (mm) of the solid core when subjected to a load of 980 N (100 kg).

#### Rebound

The initial velocity of the solid cores was measured with the same type of initial velocity instrument as used by the official regulating body—the United States Golf Association (USGA). Each rebound value shown in Table 4 is the difference between the initial velocity of the solid core obtained in that particular example and the initial velocity of the solid core obtained in Comparative Example 2.

In each example, the resulting solid core was placed in a given mold and the appropriate resin shown in Table 3 was injection-molded over the core, thereby producing an inner layer-covered core having a diameter of about 39.7 mm. The covered core was then transferred to a given mold, and the appropriate resin shown in Table 3 was injection molded over the covered core, yielding a three-piece solid golf ball having a diameter of about 42.7 mm and a weight of about 45.3 g. Trade names appearing in Table 3 are described below.

Himilan: An ionomer resin produced by DuPont-Mitsui Polychemicals Co., Ltd.

Surllyn: An ionomer resin produced by E. I. du Pont de Nemours and Co.

Dynaron: An E-EB-E block copolymer produced by JSR Corporation

Pandex: A polyurethane elastomer produced by Bayer-DIC Polymer, Ltd.

The properties of the resulting golf balls were determined as described below. The results are shown in Table 4.

#### Material Properties

The Shore D hardnesses of the inner cover layer and the outer cover layer were measured with a durometer by the test method described in ASTM D2240.

#### Golf Ball Properties

The carry and total distance were measured when the ball was hit at a head speed (HS) of 50 m/s with a driver (No. 1 Wood) mounted on a swing machine.

#### Feel

The feel of the ball when actually shot with a driver (No. 1 Wood) and putter was rated by five professional and five top-caliber amateur golfers as "Too hard," "Good" or "Too soft." The rating assigned most often to a particular ball was used as that ball's overall rating.

US 6,634,961 B2

13

TABLE 3

	A	B	C	D	E	F	G
Formulation (pbw)							
Himilan 1706	50	70					
Himilan 1605	50						
Himilan 1557						20	
Himilan 1855						30	
Himilan AM7316		12					
Surlyn 8945			35				
Surlyn 9945			35				
Surlyn 8120				100			50
Dynaron 6100P			30				
Pandex T8290					50		
Pandex T8295					50	100	
Behenic acid		16					
Magnesium oxide		2					
Titanium dioxide	4	2	4	4	2.7	2.7	4

14

Japanese patent application Ser. No. 2001-163238 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A multi-piece solid golf ball comprising a solid core, an inner cover layer and an outer cover layer, wherein the solid core is molded from a rubber composition comprising

100 parts by weight of a base rubber composed of (a) 20 to 100 wt % of a polybutadiene having a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 2%, having a viscosity  $\eta$  at 25° C. as a 5 wt % solution in toluene of up to 600 mPa·s, being synthesized using a rare-earth catalyst and satisfying the relationship:  $10B + 5 \leq A \leq 10B + 60$ , wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the polybutadiene and B is the ratio Mw/Mn between the weight-average molecular weight Mw and the number-average molecular weight Mn of the polybutadiene, in combination with (b) 0 to 80 wt % of a diene rubber other than component (a),

TABLE 4

	Example					Comparative Example			
	1	2	3	4	5	1	2	3	4
<u>Core properties</u>									
Deflection (mm) under 980 N load	3.8	3.8	3.5	3.5	3.3	3.3	3.5	3.5	3.3
Specific gravity	1.15	1.15	1.15	1.21	1.21	1.21	1.21	1.21	1.21
Rebound (m/s)	+0.9	+0.9	+1.1	+0.7	+0.8	+0.3	0	+0.5	+0.5
<u>Inner cover layer</u>									
Type	A	B	C	A	B	B	A	D	D
Shore D hardness	63	60	56	63	60	60	63	45	45
Specific gravity	0.98	0.97	0.97	0.98	0.97	0.97	0.98	0.98	0.98
Thickness (mm)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
<u>Outer cover layer</u>									
Type	E	F	F	G	G	G	G	G	A
Shore D hardness	47	51	51	53	53	53	53	53	63
Specific gravity	1.18	1.18	1.18	0.98	0.98	0.98	0.98	0.98	0.98
Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
<u>Golf ball properties</u>									
When hit with No. 1 Wood at HS of 50 m/s									
Carry (m)	227.0	226.9	226.7	226.9	226.7	223.8	222.2	217.7	220.8
Total distance (m)	258.5	258.8	258.3	258.3	258.0	255.0	253.4	248.3	252.8
Spin rate (rpm)	3205	3153	3241	3125	3180	3182	3121	3305	3177
Feel on impact	good	good	good	good	good	good	good	too soft	good
Spin rate on approach shot (sand wedge; HS 20 m/s)	6323	6251	6226	6118	6111	6107	6113	6186	4308
Feel of ball	good	good	good	good	good	good	good	too soft	too hard

## US 6,634,961 B2

15

(c) 10 to 60 parts by weight of an unsaturated carboxylic acid or a metal salt thereof or both,

(d) 0.1 to 5 parts by weight of an organosulfur compound,

(e) 5 to 80 parts by weight of an inorganic filler,

(f) 0.1 to 5 parts by weight of an organic peroxide;

the inner cover layer has a Shore D hardness of 50 to 80;

the outer cover layer has a Shore D hardness of 35 to 60; and

the outer cover layer has a lower Shore D hardness than the inner cover layer.

2. The golf ball of claim 1, wherein the diene rubber (b) includes 30 to 100 wt % of a second polybutadiene which has a cis-1,4 content of at least 60% and a 1,2 vinyl content of at most 5%, has a Mooney viscosity ( $ML_{1+4}$  (100° C.)) of not more than 55, and satisfies the relationship:

$$\eta \leq 20A - 550,$$

wherein A is the Mooney viscosity ( $ML_{1+4}$  (100° C.)) of the second polybutadiene and  $\eta$  is the viscosity of the second polybutadiene, in mPa·s, at 25° C. as a 5 wt % solution in toluene.

16

3. The golf ball of claim 1 wherein said polybutadiene (a) is synthesized by using neodymium catalyst.

4. The golf ball of claim 1 wherein said polybutadiene (a) has a Mooney viscosity ( $ML_{1+4}$ , 100° C.) of 40 to 60.

5. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 5 units.

6. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 7 units.

7. The golf ball of claim 1, wherein the outer cover layer and the inner cover layer have a difference in Shore D hardness of at least 9 units.

8. The golf ball of claim 1, wherein said ball is three-piece construction consisting of a solid core, an inner cover layer and an outer cover layer.

9. The golf ball of claim 2, wherein the second polybutadiene in component (b) is synthesized using a Group VIII catalyst.

\* \* \* \* \*

# **EXHIBIT B**



08/11/2006 17:37 FAX 202 551 1705

PAUL HASTINGS

001

381018

**Paul Hastings**

Paul, Hastings, Janofsky & Walker LLP  
875 15th Street, N.W. • Washington, DC 20005  
Telephone 202 551 1700 • facsimile 202 551 1705 • www.paulhastings.com

**FACSIMILE TRANSMISSION**

<b>to:</b>	<b>company/office:</b>	<b>facsimile:</b>	<b>telephone:</b>
Brian S. Seal	Howrey LLP	(202) 383-6610	(202) 383-6904
<b>from:</b>	<b>facsimile:</b>	<b>telephone:</b>	<b>initials:</b>
Brandon M. White	(202) 551-1705	(202) 551-1754	BMW2
<b>client name:</b>	Bridgestone Sports	<b>client matter number:</b>	70416.00002
<b>date:</b>	August 11, 2006	<b>pages (with cover):</b>	5

**comments:**

**If you do not receive all pages, please call Immediately Facsimile Center: (202) 551-1275**

*This message is intended only for the use of the individual or entity to which it is addressed, and may contain information that is privileged, confidential and exempt from disclosure under applicable law. If the reader of this message is not the intended recipient, or the employee or agent responsible for delivering the message to the intended recipient, you are hereby notified that any dissemination, distribution or copying of this communication is strictly prohibited. If you have received this communication in error, please notify us immediately by telephone, and return the original message to us at the above address via the U.S. Postal Service. Thank you.*

08/11/2006 17:37 FAX 202 551 1705

PAUL HASTINGS

002

**PaulHastings**

Paul, Hastings, Janofsky & Walker LLP  
 875 15th Street, N.W. - Washington, DC 20005  
 telephone 202 551 1700 • facsimile 202 551 1705 • www.paulhastings.com

Atlanta  
 Beijing  
 Brussels  
 Hong Kong  
 London  
 Los Angeles  
 Milan  
 New York  
 Orange County  
 Palo Alto  
 Paris  
 San Diego  
 San Francisco  
 Shanghai  
 Stamford  
 Tokyo  
 Washington, DC

(202) 551-1754  
 brandonwhite@paulhastings.com

August 11, 2006

70416.00002

VIA FACSIMILE TO (202) 383-6610

Brian S. Seal, Esq.  
 Howrey LLP  
 1299 Pennsylvania Ave., N.W.  
 Washington, DC 20004

Re: *Bridgestone Sports v. Acushnet – Designation of Accused Products*

Dear Brian:

Pursuant to paragraph 2 of the Court's August 3, 2006 Order, Bridgestone hereby designates the following Acushnet products as the accused Acushnet products:

1. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claims 1, 5 and 9 of the '652 Patent:
  - Titleist Pro V1, including golf balls made, used, sold, or offered for sale having the sidestamps ◀Pro V1 392▶ and ◀Pro V1-392▶.
  - Titleist Pro V1x, including golf balls made, used, sold, or offered for sale having the sidestamps ◀Pro V1x 332▶ and ◀Pro V1x-332▶.
  - Titleist Pro V1\*, including golf balls made, used, sold, or offered for sale have the sidestamp ◀Pro V1\* 392▶.
2. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claims 1 and 9 of the '652 Patent:
  - Titleist NXT, including golf balls made, used, sold, or offered for sale having the sidestamps ◀NXT▶ and ◀-NXT-▶.
  - Titleist NXT Tour, including golf balls made, used, sold, or offered for sale having the sidestamps ◀NXT•Tour▶, ◀NXT Tour▶ and ◀NXT-Tour▶.

LEGAL\_US\_E # 71615382.1

08/11/2006 17:37 FAX 202 551 1705

PAUL HASTINGS

003

Brian S. Scal, Esq.  
 August 11, 2006  
 Page 2

- Titleist DT So/Lo, including golf balls made, used, sold, or offered for sale having the sidestamps DT So/Lo and ◀DT So/Lo▶.
  - Titleist PTS So/Lo, including golf balls made, used, sold, or offered for sale having the sidestamps PTS So/Lo and ◀PTS So/Lo▶.
  - Pinnacle Exception, including golf balls made, used, sold, or offered for sale having the sidestamps Exception and the Exception airfoil logo.
3. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claims 1, 6 and 7 of '852 Patent:
- Titleist Pro V1, including golf balls made, used, sold, or offered for sale having the sidestamps Pro V1 392, Pro V1 392 (stretched), ◀Pro V1-392▶, ◀•Pro V1 392•▶ and ◀Pro V1-392▶.
  - Titleist Pro V1x, including golf balls made, used, sold, or offered for sale having the sidestamps ◀•Pro V1x 332•▶ and ◀Pro V1x-332▶.
  - Titleist Pro V1\*, including golf balls made, used, sold, or offered for sale have the sidestamp ◀Pro V1\* 392▶.
4. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claim 1 of the '817 Patent:
- Titleist NXT, including golf balls made, used, sold, or offered for sale having the sidestamps ◀NXT▶ and ◀-NXT-▶.
  - Titleist NXT Tour, including golf balls made, used, sold, or offered for sale having the sidestamps ◀NXT•Tour▶, ◀NXT Tour▶ and ◀NXT-Tour▶.
  - Titleist DT So/Lo, including golf balls made, used, sold, or offered for sale having the sidestamps DT So/Lo and ◀DT So/Lo▶.
  - Titleist PTS So/Lo, including golf balls made, used, sold, or offered for sale having the sidestamps PTS So/Lo and ◀PTS So/Lo▶.
  - Pinnacle Exception, including golf balls made, used, sold, or offered for sale having the sidestamps Exception and the Exception airfoil logo.

08/11/2006 17:37 FAX 202 551 1705

PAUL HASTINGS

004

Brian S. Scal, Esq.  
August 11, 2006  
Page 3

5. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claim 1 of the '707 Patent:
  - Titleist Pro V1, including golf balls made, used, sold, or offered for sale having the sidestamps Pro V1 392, Pro V1 392 (stretched) and ◀Pro V1-392▶.
6. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claim 1 of the '834 Patent:
  - Titleist NXT, including golf balls made, used, sold, or offered for sale having the sidestamps ◀NXT▶ and ◀-NXT -▶.
  - Titleist DT So/Lo, including golf balls made, used, sold, or offered for sale having the sidestamps DT So/Lo and ◀DT So/Lo▶.
  - Titleist PTS So/Lo, including golf balls made, used, sold, or offered for sale having the sidestamps PTS So/Lo and ◀PTS So/Lo▶.
  - Pinnacle Exception, including golf balls made, used, sold, or offered for sale having the sidestamps Exception and the Exception airfoil logo.
7. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claim 2 of the '961 Patent:
  - Titleist Pro V1, including golf balls made, used, sold, or offered for sale having the sidestamp ◀Pro V1-392▶.
8. The following golf balls, and all other golf balls made, used, sold, or offered for sale by Acushnet under a different brand or sidestamp and being substantially identical to any of the following golf balls, infringe claims 11, 13, 16 and 26 of the '791 Patent:
  - Titleist Pro V1, including golf balls made, used, sold, or offered for sale having the sidestamps ◀Pro V1 392▶ and ◀Pro V1-392▶.
  - Titleist Pro V1x, including golf balls made, used, sold, or offered for sale having the sidestamps ◀Pro V1x 332▶ and ◀Pro V1x-332▶.



08/11/2006 17:38 FAX 202 551 1705

PAUL HASTINGS

005

Brian S. Seal, Esq.  
August 11, 2006  
Page 4

Please let me know if you have any questions.

Sincerely,

A handwritten signature in black ink, appearing to read "Brandon M. White", with a long horizontal line extending to the right.

Brandon M. White  
for PAUL, HASTINGS, JANOFSKY & WALKER LLP

# **EXHIBIT C**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**

# **EXHIBIT D**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**



# **EXHIBIT E**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**

# **EXHIBIT F**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**



# EXHIBIT G

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**

# **EXHIBIT H**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**

# **EXHIBIT I**



Westlaw.

Not Reported in F.Supp.2d

Page 1

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

P

PharmaStem Therapeutics, Inc. v. ViaCell, Inc.  
D.Del., 2004.

Only the Westlaw citation is currently available.

United States District Court, D. Delaware.  
PHARMASTEM THERAPEUTICS, INC.,  
Plaintiff,

v.

VIACELL INC., et al., Defendants.  
No. C.A. 02-148 GMS.

Sept. 15, 2004.

Philip A. Rovner, of Potter Anderson & Corroon LLP, Wilmington, Delaware, for Plaintiff, Paul J. André, Lisa Kobialka, of Perkins Coie LLP, Menlo Park, California, of counsel.

Jeffrey L. Moyer, of Richards Layton & Finger, Wilmington, Delaware, Richard D. Kirk, of Morris James Hitchens & Williams LLP, Wilmington, Delaware, and Robert F. Stewart, of Dilworth Paxson LLP, Wilmington, Delaware, for Defendants, Paul F. Ware, John C. Englander, James C. Rehnquist, James W. McGarry, and Elaine Herrmann Blais, of Goodwin Procter LLP, Boston, Massachusetts; William F. Abrams, Thomas F. Chaffin, and Randal Ivor-Smith, of Pillsbury Winthrop LLP, Palo Alto, California; and James L. Rodgers, Evelyn H. McCarthy, and Lisa Burgin Conte, of Dilworth Paxson LLP, Philadelphia, Pennsylvania, of counsel.

#### MEMORANDUM OPINION

SLEET, J.

#### I. INTRODUCTION

\*1 On February 22, 2002, PharmaStem Therapeutics, Inc. ("PharmaStem") filed suit against ViaCell, Inc. ("ViaCell"), Cryo-Cell International, Inc. ("Cryo-Cell"), CorCell, Inc. ("CorCell"), StemCyte, Inc. ("StemCyte"), CBR Systems, Inc. ("CBR"), Birthcells Technology, Inc. ("Birthcells"), Nustem Technologies, Inc. ("Nustem"), and Bio-Cell, Inc. ("Bio-Cell") (collectively "ViaCell" or "the defendants"),<sup>FN1</sup> alleging infringement of United States Patents Nos. B1 5,004,681 (" '681 Patent") and 5,192,553 (" '553 Patent") (collectively "the Patents-In-Suit"). The Patents-In-Suit are generally directed toward cryopreserved therapeutic compositions containing hematopoietic stem cells obtained from umbilical cord or placental blood of a newborn, the '681 Patent, and methods pertaining to the therapeutic use of such compositions, the '553 Patent.

FN1. A default judgment was subsequently rendered against NuStem on July 10, 2002. StemCyte and PharmaStem entered a settlement agreement before trial, and StemCyte accordingly was dismissed from this action on October 21, 2003.

ViaCell asserted the defenses of invalidity for anticipation, indefiniteness, inequitable conduct and obviousness. The court held a *Markman* hearing and issued an order construing the disputed terms of the '681 and '553 Patents on January 13, 2003. A jury trial commenced on October 10, 2003. During trial, both parties properly moved for judgment as a matter of law ("JMOL") pursuant to Rule 50(a) of the Federal Rules of Civil Procedure. The court reserved ruling on all JMOL motions.

On October 29, 2003, the jury returned a unanimous verdict on all claims in favor of PharmaStem. The jury found that each of the defendants infringed the claims of the '681 and '553 Patents, and that each of the defendant's infringement of those patents was willful. The jury also upheld the validity and enforceability of the Patents-In-Suit, found that PharmaStem did not commit any anti-trust violation, and awarded PharmaStem past damages in the amount of \$7,126,544.92. The court entered judgment on the verdict on October 30, 2003.

© 2007 Thomson/West. No Claim to Orig. U.S. Govt. Works.

Not Reported in F.Supp.2d

Page 2

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

Following the jury's verdict, ViaCell filed a renewed motion for judgment as a matter of law, and, in the alternative, a motion for a new trial or for a remittitur. Defendants CBR, CorCell, and Cryo-Cell joined in Viacell's motions and submitted individual memoranda addressing issues specific to each of them. ViaCell filed another alternative motion, in which the three other defendants also joined, for findings by the court and/or to alter or amend judgment pursuant to Federal Rule of Civil Procedure 52, 59(e) and/or the court's equitable power. PharmaStem filed a motion for enhanced damages, attorneys' fees, pre-judgment interest and post judgment interest, a motion for a permanent injunction, as well as a motion to strike the affidavit of Chris Adams submitted in support of ViaCell's motion to alter or amend the judgment. Addressing these motions collectively herein, the court will enter judgment as a matter of law that defendants do not infringe the '553 patent and grant a partial new trial on the issue of infringement of the '681 Patent.

## II. STANDARDS OF REVIEW

### A. Renewed Motion for Judgment as a Matter of Law

\*2 Pursuant to Federal Rule of Civil Procedure 50, a court may render judgment as a matter of law after the moving party is fully heard on an issue at trial, if "there is no legally sufficient evidentiary basis for a reasonable jury to find for that party on that issue." *Walter v. Holiday Inns, Inc.*, 985 F.2d 1232, 1238 (3d Cir.1993) (citation omitted). If the court denies a motion for JMOL during trial, the motion may be renewed within ten days of entry of judgment in the case. Fed. R. Civ. P. 50(b). To prevail on a renewed motion for JMOL following a jury trial, a party "must show that the jury's findings, presumed or express, are not supported by substantial evidence or, if they were, that the legal conclusion(s) implied [by] the jury's verdict cannot in law be supported by those findings." *Pannu v. Iolab Corp.*, 155 F.3d 1344, 1348 (Fed.Cir.1998) (quoting *Perkin-Elmer Corp. v. Computervision Corp.*, 732 F.2d 888, 893 (Fed.Cir.1984)). "Substantial" evidence is such relevant evidence from the record taken as a whole

as might be accepted by a reasonable mind as adequate to support the finding under review." *Perkin-Elmer Corp.*, 732 F.2d at 893. In assessing the sufficiency of the evidence, the court must draw all reasonable inferences from the evidence in the light most favorable to the nonmovant. *Id.*; *Richardson-Vicks Inc. v. Upjohn Co.*, 122 F.3d 1476, 1479 (Fed.Cir.1997). The appropriate inquiry is whether a reasonable jury, given the facts before it, could have arrived at the conclusion it did. *Dawn Equip. Co. v. Kentucky Farms, Inc.*, 140 F.3d 1009, 1014 (Fed.Cir.1998). The court may not determine the credibility of the witnesses nor "substitute its choice for that of the jury between conflicting elements of the evidence." *Perkin-Elmer Corp.*, 732 F.2d at 893.

### B. Motion for a New Trial

The court may grant a new trial pursuant to Federal Rule of Civil Procedure 59 "for any of the reasons for which new trials have heretofore been granted in actions of law in the courts of the United States." Fed. R. Civ. P. 59(a). A court should grant a new trial in a jury case, however, only if "the verdict was against the weight of the evidence ... [and] a miscarriage of justice would result if the verdict were to stand." *Williamson v. Consolidated Rail Corp.*, 926 F.2d 1344, 1352 (3d Cir.1991). In making this determination, the trial judge should consider the overall setting of the trial, the character of the evidence, and the complexity or simplicity of the legal principles which the jury had to apply to the facts. *Lind v. Schenley Industries, Inc.*, 278 F.2d 79, 89 (3d Cir.), cert. denied, 364 U.S. 835 (1960)

## III. DISCUSSION

### A. Defendants' Renewed Motion for Judgment as a Matter of Law

#### 1. The Jury's Verdict That the Patents-In-Suit Are Not Obvious, Anticipated or Indefinite Is Supported by Substantial Evidence.

##### a. Obviousness

© 2007 Thomson/West. No Claim to Orig. U.S. Govt. Works.

Not Reported in F.Supp.2d

Page 3

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

The defendants contend that both the '681 and '553 Patents are invalid as obvious under 35 U.S.C. § 103. Whether or not a patent is obvious over the prior art is a question of law. See *Richardson-Vicks v. Upjohn Co.*, 122 F.3d 1479, 1479 (Fed Cir.1997); see also *Karsten Mfg. Corp. v. Cleveland Golf Co.*, 242 F.3d 1376, 1384-85 (Fed Cir.2001). Section 103 provides:

\*3 A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains.

35 U.S. § 103. Put simply, an invention is invalid if "the difference between the new thing and what was known before is not considered sufficiently great to warrant a patent." *Graham v. John Deere Co.*, 383 U.S. 1, 15 (1966). Obviousness cannot be based on "the hindsight combination of components selectively culled from the prior art to fit the parameters of the invention." *ADT Corp. v. Lydall, Inc.*, 159 F.3d 534, 546 (Fed Cir.1998). The Supreme Court has set forth four factors relevant to determining obviousness: (1) the scope and content of the prior art; (2) the differences between the claimed invention and the prior art; (3) the level of ordinary skill in the art; and (4) other secondary considerations. *Graham*, 383 U.S. at 17-18. Evaluating the *Graham* factors in view of the evidence adduced at trial, it was not unreasonable for the jury to have concluded that the Patents-In-Suit were not obvious.

Indeed, PharmaStem proffered ample evidence to support the jury's verdict. Both a suggestion to make the composition or carry out the claimed process and a reasonable expectation of success must be found in the prior art to support a conclusion that a patent is obvious. See *In re Vaeck*, 947 F.2d 488, 493 (Fed.Cir.1991). At trial, PharmaStem presented testimony that there were problems associated with transplant tissues used prior to the Patents-In-Suit. Bernstein Tr. at 2035-2038. There was also tremendous skepticism

in the transplant field regarding the use of cord blood as a transplant tissue, Bernstein Tr. at 2043-204, and the references. ViaCell asserts (namely Koike, Knudtson and Vidal) did not overcome this skepticism. Bernstein Tr. at 2045-2048, 2054-2060. Finally, testimony established that those in the field of transplantation were surprised at the result of the first cord blood transplant conducted by the inventors of the Patents-In-Suit. Bernstein Tr. at 2061-2062. See also Wagner Tr. at 1378-1379. It is true that ViaCell capably highlights record evidence as to the meaning one of ordinary skill would attach to the alleged prior art references. Base upon the record evidence, a jury could have found that the Patents-In-Suit were obvious. This jury, however, did not, and the aforementioned evidence provided it with sufficient basis to reach the conclusion that, prior to the inventions of the Patents-In-Suit, those in the field of hematopoietic reconstitution would not have expected cord blood to be a successful transplant tissue.

The jury also received an abundance of evidence to support the secondary considerations of long felt need, commercial success, failure of others, copying, and unexpected results. See e.g., Bernstein Tr. at 2036, 2060-2061; Wagner Tr. at 1187; Tr. Ex. 413. Additionally, with respect to the '681 patent; the jury was permitted to consider the fact that the Patent and Trademark Office ("PTO") considered the alleged prior art in the reexamination and ultimate reissue of that patent. Similarly, during examination of the '553 Patent, the PTO considered the Ende, Prindull, and Knudtson references, a fact which the jury was also entitled to consider in evaluating their combined effect on the obviousness issue. The court is not to "substitute its choice for that of the jury between conflicting elements of the evidence." *Perkin-Elmer Corp.*, 732 F.2d at 893. In view of this standard, there is no basis to overturn the jury's finding that the Patents-In-Suit are not obvious.

#### b. Anticipation

\*4 Likewise, the jury's finding that the Patents-In-Suit are not invalid for anticipation is

Not Reported in F.Supp.2d

Page 4

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

supported by substantial evidence. The defendants first contend that the '681 patent is anticipated by Koike because the latter discloses each limitation of the former's claims. "An anticipating reference must describe the patented subject matter with sufficient clarity and detail to establish that the subject matter existed in the prior art and that such existence would be recognized by persons of ordinary skill in the field of the invention." The '681 Patent claims a cryopreserved therapeutic composition comprising "viable human neonatal or fetal hematopoietic stem cells derived from the umbilical cord blood or placental blood of a single human collected at the birth of said human, in which said cells are present in an amount sufficient to effect hematopoietic reconstitution of a human adult." To anticipate the '681 Patent, Koike must demonstrate that stem cells were present in umbilical cord blood. There is ample evidence in the record establishing that Koike did not demonstrate stem cells. For example, Dr. Wagner's cross examination testimony stated that Koike did not prove that there were stem cells in umbilical cord blood.<sup>FN2</sup> Wagner Tr. at 1333. Dr. Bernstein also testified that the reference does not teach stem cells nor a therapeutic composition for use in hematopoietic reconstitution. Bernstein Tr. at 2053. In this regard, the jury's verdict that the '681 patent is not anticipated by Koike is supported by substantial evidence so as to preclude judgment as a matter of law on the issue of anticipation.

FN2. Dr. Wagner's cross testimony could be further construed to support the conclusion that Koike did not cryopreserve enough cord blood, or teach cryopreservation of enough cord blood, for hematopoietic reconstitution of a human, whether adult or child, which is another limitation of the '681 Patent's claims. See Wagner Tr. at 1342-1343.

The court reaches the same conclusion with respect to the '553 Patent. The '553 Patent claims in pertinent part:

A method for hematopoietic or immune reconstitution of a human comprising:

(a) isolating human neonatal or fetal blood components containing hematopoietic stem cells;

(b) cryopreserving the blood components; and  
(c) introducing the blood components into a suitable human host.

It is undisputed that Koike did not introduce cord blood into a human, which is a necessary limitation of the '553 Patent. The defendants claim that Koike's suggestion that introducing the stem cells into a human host should be done is a sufficiently enabling disclosure to warrant a finding of anticipation. Even so, the record contains substantial evidence from which a jury could find that a person of ordinary skill in the art would not have been so enabled. For example, Dr. Wagner testified that Koike did not do a transplant, Wagner Tr. at 1333, and Dr. Bernstein testified that Koike does not introduce stem cells into a human or teach hematopoietic reconstitution, Bernstein Tr. at 2053-2054. Again, the jury's finding that the Patents-In-Suit are not anticipated<sup>FN3</sup> is supported by substantial evidence and the court will not overturn it on this basis.

FN3. Given the absence of record evidence showing that Koike's compositions contained an amount of stem cells sufficient to effect hematopoietic reconstitution of a human adult, the defendants' inherent anticipation theory is an equally unpersuasive basis on which to enter judgment as a matter of law on this issue. Although recognition of an element in the prior art before the critical date is not necessary, inherent anticipation still requires that the element necessarily be present. *Schering Corp. v. Geneva Pharms.*, 339 F.3d 1373, 1377 (Fed.Cir.2003).

#### c. Indefiniteness

The defendants also argue that the '681 Patent is invalid because it is indefinite. Claim 1 of that patent covers "stem cells" "in an amount sufficient to effect hematopoietic reconstitution of a human adult." According to the defendants, this language is indefinite as a matter of law because it is specifically drawn to an amount of stem cells, but



Not Reported in F.Supp.2d

Page 5

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

the patent is completely silent as to a quantity. In this regard, they claim that it does not provide sufficient notice of the scope of the invention. The court is not persuaded.

\*5 Section 112 provides in pertinent part:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

35 U.S.C. § 112. The statute requires the patentee to provide the public with clear notice of what activities infringe the patent. See *Exxon Research & Eng'g Co. v. United States*, 265 F.3d 1371, 1375 (Fed.Cir.2001); *Morton Int'l v. Cardinal Chem. Co.*, 5 F.3d 1464, 1470 (Fed.Cir.1993). "If the claims, read in light of the specifications, reasonably apprise those skilled in the art both of the utilization and scope of the invention, and if the language is as precise as the subject matter permits, the courts can demand no more." *Shatterproof Glass Cor. v. Libbey-Woens Ford Co.*, 758 F.2d 613, 624 (Fed.Cir.1985) (citing *Georgia Pacific Corp. v. United States Plywood Corp.*, 258 F.2d 124, 136 (2d Cir.1958)). Indefiniteness is a question of law for the court. In *re Jolly*, 172 F.2d 566, 570 (C.C.P.A.1949); see also *Union Pacific Res. Co. v. Chesapeake Energy Corp.*, 236 F.3d 684, 692 (Fed.Cir.2001). "In a jury trial, if there are disputed factual issues related to indefiniteness, they may be submitted to the jury for resolution." *Union Carbide Chems. & Plastics Tech. Corp. v. Shell Oil Co.*, Nos. 99-274(SLR), 99-876(SLR), 2004 WL 1305849, \*10 (D.Del.2004) (citing *BJ Services Co. v. Halliburton Energy Serv., Inc.*, 338 F.3d 1368, 1372 (Fed.Cir.2003)). Because a patent is presumed valid, the party asserting a defense of invalidity on the basis of claim indefiniteness bears the burden of proof by clear and convincing evidence. See *Orthokinetics, Inc. v. Safety Travel Chairs, Inc.*, 806 F.2d 1565, 1575-76 (Fed.Cir.1986).

It is true that the language of the '681 Patent does not specify an amount of progenitor cells nor a

volume of cord blood, and the specification is silent as to a precise amount. However, these facts do not necessarily dictate that Claim 1 must fail for indefiniteness. Given that there is no determinate or determinable minimum amount of cord blood for therapeutic usefulness in humans, the record supports that the '681 Patent's claim language is as precise as the subject matter permits. Moreover, the record contains evidence establishing that a person of skill in the art would have understood what an amount of cord blood stem cells sufficient to effect hematopoietic reconstitution of a human adult means. See *Andrew Corp. v. Gabriel Electronics, Inc.*, 847 F.2d 819, 823 (Fed.Cir.1988); *Hybritech Inc. v. Monoclonal Antibodies, Inc.*, 802 F.2d 1367, 1385 (Fed.Cir.1986). Dr. Moore, PharmaStem's expert on hematopoiesis, testified that the Patents-In-Suit provide the reader with ample information to determine the amount of cord blood needed for transplantation in adults or children, and that the scientific community has in fact performed numerous transplants into adults. Moore Tr. at 340-348; see also Harris Tr. at 635-636 (for defendants' witness skilled in art stating that an amount sufficient for usefulness in a clinical setting would be "a sample that contained enough of those cells for a successful transplant"). Thus, the court can find no basis to overturn the jury's verdict that the '681 Patent is not invalid for indefiniteness.

## 2. The Jury's Verdict That the Defendants Contributorily Infringe the '553 Patent Cannot Stand.

\*6 The defendants claim that PharmaStem did not prove that they contributorily infringed the '553 Patent in that PharmaStem failed to adduce evidence that any of them sold or offered to sell cryopreserved cord blood to a transplantor or that cryopreserved cord blood was used by a single entity or group of entities acting in concert or working together to infringe the patent. The court agrees. Relevantly, the claim language of the '553 Patent requires:

A method for obtaining human neonatal or fetal hematopoietic stem or progenitor cells comprising:  
(a) isolating human neonatal or fetal blood components containing hematopoietic stem or



Not Reported in F.Supp.2d

Page 6

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

progenitor cells;  
(b) cryopreserving the blood components; and  
(c) thawing the blood components, such that the stem or progenitor cells are viable.

Because none of the defendants thaw or inject cord blood, both required elements of the '553 Patent's claims, there can be no literal infringement of the '553 Patent.

PharmaStem would, however, still be entitled to a finding of infringement if the jury reasonably could have found that the defendants contributorily infringed the '553 patent. *See* 35 U.S.C. § 271(c).

Section 271(c) states:

Whoever offers to sell or sells within the United States or imports into the United States a component of a patented machine, manufacture, combination or composition, or a material or apparatus for use in practicing a patented process, constituting a material part of the invention, knowing the same to be especially made or especially adapted for use in an infringement of such patent, and not a staple article or commodity of commerce suitable for substantial noninfringing use, shall be liable as a contributory infringer.

35 U.S.C. § 271. The verdict form required the jury to answer three questions in the affirmative in order to find that any of the defendants contributorily infringed the '553 patent. Consistent with the appropriate legal standard, the jury was required to find that (i) "cryopreserved cord blood has no substantial noninfringing use," (ii) "defendants and transplant physicians are acting in concert or working together to complete the process of infringement of claims 13, 19, 47, or 57 of the '553 patent by performing each and every one of the steps in any of those claims," and (iii) "a Defendant has contributorily infringed the '553 patent by selling or offering to sell cryopreserved cord blood that was actually used by a third party in the direct infringement of any of claims 13, 19, 47, 53, or 57 of the '553 patent." Jury Verdict Form, Qtn. Nos. 3, 4, and 5.

PharmaStem correctly points out the existence of evidence to support the jury's affirmative answer to

questions (i) and (ii) of the verdict form. The record supports a conclusion that cryopreserved cord blood is, predominantly, useful only for transplantation therapy, or the use covered by the '553 Patent. Indeed, PharmaStem adduced evidence by which a jury reasonably could have found that cord blood was viewed as medical waste prior to the inventions of the Patents-In-Suit. *See, e.g.,* Moore Tr. at 328; Broxmeyer Tr. at 365; Wagner Tr. 1195-1196.

\*7 Moreover, the jury also could have reasonably found that each of the defendants worked together with transplant physicians to complete the patented process of the asserted claims of the '553 Patent. At trial, PharmaStem adduced evidence that the defendants test the blood samples to ensure each one is sufficient for transplantation and thereby aid transplant physicians. Tr. Ex. 103; Tr. Ex. 96; Laleman Tr. at 659. The defendants marketing materials also indicate that they work with physicians in various capacities to effectuate the transplantation process. For example, CorCell's website states "CorCell and Community Blood Services (CBS) has formed a strategic partnership devoted to expertly testing, processing and storing quality cord blood stem cells for future transplantation." Tr. Ex. 516. ViaCell's founder, Cynthia Fisher, testified that the company's mission was "to provide a niche application area between the obstetrician, the Hem/Onc and the blood banking center, as far as enabling providing cord blood stem cell banking." Fisher Tr. at 707. Cryo-Cell advertises that the units of cord blood stem cells stored at its facility are transplant-ready. Tr. Ex. 98. In addition, PharmaStem presented evidence that each of the defendants has at least one representative who liaises in some capacity with transplant physicians, i.e., Dr. Goldberg of CorCell and Dr. O'Neil of Cryo-Cell. CBR designates a Director of the Facility to oversee procedures regarding the release of cord blood units for transplantation. Tr. Ex. 110. Viacell seeks advice and counsel on nucleated cell counts and volumes useful for transplantation from its Medical Scientific Advisory Board, on which five of the seven members are prominent transplant doctors or physicians with extensive experience in hematology, oncology, and/or transfusion medicine. Tr. Ex. 253, Tr. at 1461-63; *see also* Wagner Tr. at

Not Reported in F.Supp.2d

Page 7

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

1389. Finally, there is also evidence in the record showing that each of the defendants maintain records and/or other materials regarding its cord blood units which it releases to physicians to assist the transplantation process. CorCell maintains records on the cord blood units it releases, Tr. Ex. 274, and requests feedback from the transplant facility as part of its standard operating procedures, Tr. Ex. 215. Cryo-Cell provides directions to transplant physicians on how to thaw the cryopreserved cord blood unit it provides. Tr. Ex. 97. CBR has a similar document setting forth the detailed protocol between CBR and the transplant physician when a cord blood unit is requested and released. Tr. Ex. 110. In view of this evidence, it was not unreasonable for the jury to have found that the defendants and transplant physicians worked together to infringe the '553 patent.

Nevertheless, with respect to the third question on the verdict form, there is simply no evidence in the record to support the jury's affirmative answer. It is undisputed that the defendants do not own the cord blood units. Rather the units are owned by the clients, or families, and the defendants in turn provide services with respect to the processing and storing of the compositions. Although the defendants charge enrollment, processing, and banking fees with respect to their storage services, they do not *sell* or *offer to sell* the cord blood units. Indeed, the record evidence on this issue is clear that the defendants sell a service, not cord blood units. See Hendrix Tr. 1042; Tr. 2653; Wagner Tr. 1278.

\*8 Tellingly, PharmaStem cannot direct the court to a single fact in evidence that would support a finding that any of the defendants sell or offer to sell cord blood. PharmaStem attempts to overcome this deficiency in the record by arguing that Section 271(c) focuses on the financial benefit derived by the seller regardless of the source. But the statute could not be clearer. Section 271(c) liability is clearly dependant upon the accused infringer's selling or offering to sell a component of the patented process, here cord blood units. See 35 U.S.C. § 271(c). Drawing all reasonable inferences from the evidence in favor of PharmaStem, the court agrees with the defendants that the jury's

finding on the element of contributory infringement is not supported by substantial evidence. In this regard, the jury's verdict on contributory infringement cannot stand. The court finds as matter of law that the defendants' services do not infringe the '553 patent.<sup>FN4</sup>

FN4. Because the court finds that the defendants do not infringe the '553 Patent, it will not address the issue of willful infringement with respect to that patent.

#### B. Defendants' Motion for a New Trial

The defendants alternatively contend that the court should set aside the judgment and grant a new trial because the jury's verdict was against the great weight of the evidence. The court agrees with respect to the jury's finding that the 100% of the defendants' cord blood units infringe the '681 patent and accordingly will grant a partial new trial on this issue.

##### 1. Inventorship

The defendants first claim that a new trial is warranted because the great weight of the evidence established that the Patents-In-Suit are invalid for failure to name one of the inventors, Dr. Pablo Rubinstein. The court does not agree.

Every patent receives the presumption that its inventors are the true and only inventors. See e.g., *Acromed Corp. v. Sofamor Danek Grp., Inc.*, 253 F.3d 1371, 1379 (Fed.Cir.2001). Invalidity for failure to name an inventor must be established by clear and convincing evidence. See *id.* at 1379. To be a joint inventor, one must "contribute in some significant manner to the conception of the invention." *Fina Oil & Chem. Co. v. Ewen*, 123 F.3d 1466, 1473 (Fed.Cir.1997). Specifically, each person claiming to be an inventor must have contributed to the conception of the invention. *Acromed*, 253 F.3d at 1379. Beyond conception, the purported inventor must demonstrate that he made "a contribution to the claimed invention that is not insignificant in quality, when contribution is

Not Reported in F.Supp.2d

Page 8

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

measured against the dimension of the full invention, and [did] more than merely explain to the real inventors well-known concepts and/or the current state of the art." *Id.* at 1379.

Although the defendants point to evidence from which a jury could have found Dr. Rubinstein's contributions to be significant, PharmaStem adduced at least an equal amount of evidence that his contribution did not rise to the level of inventorship. Indeed, a jury could conclude from the record that Dr. Rubinstein provided consultation on cryopreservation methods which were already available in the art. *See* Bernstein Tr. at 1176-1177. Moreover, Dr. Rubinstein admitted that he published his cryopreservation techniques more than one year prior to the inventions of the Patents-In-Suit, Rubinstein Tr. at 1176-1177, which would allow a jury to conclude that any contribution he made was rendered prior art by the time of the patenting of the invention. *See* 35 U.S.C. § 102; *Hess v. Advanced Cardiovascular Sys.*, 106 F.3d 976, 981 (Fed.Cir.1997). In light of these significant pieces of evidence supporting the jury's finding that Dr. Rubinstein was not improperly omitted as an inventor, the court finds no basis to grant a new trial on the issue of invalidity for failure to name an inventor.

## 2. Inequitable Conduct

\*9 The defendants also argue that the jury's finding that PharmaStem did not engage in inequitable conduct before the PTO in the procurement of the '681 and '553 Patents is against the great weight of the evidence. The court, however, is not persuaded that the jury's finding on this issue warrants a new trial. The burden is on the party seeking to invalidate the patents to prove inequitable conduct by clear and convincing evidence. In view of the defendants' burden, the jury's verdict was not against the great weight of the evidence.

As evidence of PharmaStem's alleged inequitable conduct, the defendants point to the PharmaStem's failure to disclose two pieces of information to the PTO. First, after PharmaStem had presented its arguments to the PTO in reexamination, but several

months before the '681 Patent reissued, the European Patent Office ("EPO") denied PharmaStem's European counterpart application, rejecting its argument that Koike does not teach stem cells. PharmaStem did not bring the EPO's rejection of its argument to the attention of the PTO before reissue. Second, in its opinion, the EPO cites the 1997 Broxmeyer article for the proposition that relevant scientific community considered progenitor cell assays to be reliable assays for stem cells. In view of these facts, the defendants argue that the jury's finding that PharmaStem did not engage in inequitable conduct before the PTO is against the great weight of the evidence.

"One who alleges inequitable conduct arising from a failure to disclose prior art must offer clear and convincing proof of the materiality of the prior art, knowledge chargeable to the applicant of that prior art and of its materiality, and the applicant's failure to disclose the prior art, coupled with an intent to mislead the PTO." *Molins*, 48 F.3d at 1178; *accord Rockwell Techs., LLC v. Spectra Physics Lasers, Inc.*, 2002 WL 531555, at \*3 (D.Del. Mar. 26, 2002). "Materiality and intent to deceive are distinct factual inquiries, and each must be shown by clear and convincing evidence." *Life Techs., Inc. v. Clontech Labs., Inc.*, 224 F.3d 1320, 1324 (Fed.Cir.2000); *accord Isco Int'l, Inc. v. Conductus, Inc.*, 2003 WL 22006253, at \*6 (D.Del. Aug. 21, 2003). Patent applicants have a duty to disclose to the PTO "any material prior art or other information cited or brought to their attention in any related foreign application." Manual of Patent Examining Procedure § 2001.06(a) (4th ed., rev.8, Oct. 1981). However, a finding of inequitable conduct for nondisclosure of information requires proof that the applicant made a deliberate decision to withhold a known material reference from the PTO. *See Molins PLC v. Textron, Inc.*, 48 F.3d 1172, 1181 (Fed.Cir.1995).

Given the controlling standards, PharmaStem adduced significant evidence to rebut the defendants' inequitable conduct case. Specifically, the EPO's decision applied European, as opposed to United States, patent laws, and examined different claims than the ones at issue before the PTO in the reexamination. Tr. Ex. 1013. Moreover, there is no



Not Reported in F.Supp.2d

Page 9

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

dispute that PharmaStem disclosed Koike to the PTO in the reexamination, and that the PTO came to its own conclusion as to what the reference taught. With respect to the Broxmeyer article, it was published nearly ten years after the initial filing of the Patents-In-Suit, and therefore not a prior art reference. Tr. Ex. 1015. Further lending credence to PharmaStem's view that the article was not material, the EPO characterized the Broxmeyer article as "indirect evidence" and cited it in the portion of the opinion on novelty, which was not at issue in the reexamination before the PTO. Tr. Ex. 1013. When viewed as a whole, the record more than supports a conclusion that PharmaStem did not possess the requisite intent to deceive the PTO and therefore did not engage in inequitable conduct.

### 3. Infringement of the '681 Patent

#### a. Dr. Hendrix's Testimony

\*10 As one of the bases for their motion for a new trial on infringement of the '681 Patent, the defendants contend that Dr. Mary Hendrix, PharmaStem's infringement expert, should not have been permitted to testify. During the pretrial stage of proceedings, the defendants objected to Dr. Hendrix's testimony in a motion *in limine* and then again at the close of trial moved to strike the doctor's testimony. The court denied both of these motions, but will revisit its rulings in light of the evidentiary record now before it.

Rule 702 has three requirements as to expert opinions: 1) the witness must be an expert; (2) the witness must testify to scientific, technical, or other specialized knowledge; and 3) the testimony must assist the trier of fact. See *United States v. Velasquez*, 64 F.3d 844, 849 (3d Cir.1995) (citations omitted). The U.S. Supreme Court's decision in *Daubert v. Merrell Dow Pharmaceuticals*, 509 U.S. 579 (1993), established a gatekeeping role for trial court judges in determining the admissibility of expert testimony on scientific evidence. When an expert bases opinion testimony on scientific knowledge, the testimony will not be admitted unless it is derived by the

scientific method and is supported by "appropriate validation." *Daubert*, at 590. This standard of evidentiary reliability focuses on the scientific validity of the expert's methods rather than the soundness of his specific conclusions. *Id.* at 589 ("[the] inquiry into the reliability of scientific evidence .... requires a determination as to its scientific validity."); see also *Oddi v. Ford Motor Co.*, 234 F.3d 136, 145 (3d Cir.2000); *United States v. Shea*, 957 F.Supp. at 337. An expert's opinion is reliable if it is based on the "methods and procedures of science" rather than on "subjective belief or unsupported speculation"; the expert must have "good grounds" for his or her belief. See *Daubert*, 509 U.S. at 589.

The defendants contend that the subject of Dr. Hendrix's testimony was not one for which expertise was necessary in that she based her infringement opinion entirely on an analysis of the defendants' marketing materials, without ever considering any data regarding the composition of the defendants' cord blood units. Dr. Hendrix is an accomplished stem cell biologist, but is not qualified as an expert in marketing or advertising. Moreover, her so-called analysis of the defendants' marketing materials was well within the jury's common knowledge, common sense and common experience. See *United States v. Stevens*, 935 F.2d 1380, 1399-1400 (3d Cir.1991) (upholding Federal Rule of Evidence 403 exclusion of expert testimony regarding eye witness identification where the evidence was susceptible of elucidation without specialized knowledge and jury could have ascertained through common sense). In view of these considerations, the court is persuaded that Dr. Hendrix's conclusion, evidenced in her expert report and adduced through her testimony, that 100% of the defendants' cord blood units infringe the '681 Patent was based upon a legally improper methodology that was unreliable as a matter of law under *Daubert*.

\*11 Significantly, Dr. Hendrix admitted that she did not review or analyze any of the defendants' cord blood samples in reaching her opinion. Hendrix Tr. at 1038. Moreover, she explicitly testified that her opinion that all of the defendants' cord blood units infringe the '681 Patent was based on the fact that the defendants "promise stem cells

Not Reported in F.Supp.2d

Page 10

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

for pediatric and adult transplantation." Hendrix Tr. at 1021. In this regard, her opinions are not based upon any methods or procedures of science in general and certainly not upon her specific expertise as a stem cell biologist, no matter how knowledgeable she may have been in that field. The court therefore determines that her opinion of infringement is no more than a lay-person's interpretation of the defendants' marketing materials. The materials relied upon by Dr. Hendrix may be persuasive on the issue of infringement, but permitting PharmaStem to couch its presentation of this evidence in the form of an expert opinion was an error.

b. The Lack of Record Evidence that 100% of the Defendants' Units Infringe the '681 Patent

Claim 1 of the '681 Patent covers compositions containing stem cells "in an amount sufficient to effect hematopoietic reconstitution of a human adult." To prove infringement, therefore, PharmaStem was required to adduce evidence that the defendants cord blood units contained an amount of stem cells sufficient for transplantation into an adult. In the absence of Dr. Hendrix's testimony, the record is void of any proof to support a finding that 100% of the defendants' cord blood units infringe the '681 Patent. To the contrary, the record overwhelmingly indicates that cord blood units will *not all* contain sufficient cells to reconstitute an adult. *See* Wagner Tr. at 1270; *see also* Tr. Ex. 1370 at 30 (PharmaStem telling the PTO that cord blood units "are highly variable in their stem cell content such that any particular cord blood collection may have low or no stem cells"). The jury's finding that *all* of the defendants' cord blood units infringe the '681 Patent, consequently, was against the great weight of the evidence.

At the same time, however, the record suggests that at least some of the defendants' cord blood units infringe in that there is evidence of successful transplants of the defendants' compositions into human adults. *See, e.g.*, Tr. Ex 115 (circumstantial evidence in the form of statements on CBR's website that a "newborn's cord blood stem cells were transplanted to her mother to treat chronic

myelogenous leukemia," and that other transplants have occurred for the newborn's mother father and cousin); Tr. Ex. 103 (draft of ViaCord's private placement memorandum acknowledging that adult transplants have occurred). As a result, the court will grant a new trial, excluding Dr. Hendrix's expert testimony, on the issue of infringement of the '681 Patent and the resultant damages therefrom. <sup>FN5</sup>

FN5. Again, in light of its granting a new trial on the infringement issue, the court will not rule on the issue of willful infringement with respect to the '681 Patent

#### IV. CONCLUSION

For the aforementioned reasons, the court will enter judgment as a matter of law that the defendants do not infringe the '553 Patent and grant a new trial on the issue of infringement and damages with respect to the '681 Patent. In all other aspects, the motions filed by the parties are denied. An order to this effect will accompany this opinion.

#### ORDER

\*12 For the reasons set forth in the court's memorandum opinion issued contemporaneously herewith, IT IS HEREBY ORDERED that:

1. Joint Renewed Motion by ViaCell, Inc, Cyro-Cell, Inc, CorCell, Inc, CBR Systems, Inc. for Judgment as a Matter of Law or in the Alternative, for a New Trial (or for Remittitur) (D.I.448) is GRANTED IN PART.
2. PharmaStem, Inc.'s Motion for Enhanced Damages, Attorneys' Fees, Pre-Judgment Interest and Post Judgment Interest (D.I.446) is DENIED.
3. PharmaStem, Inc.'s Motion for a Permanent Injunction (D.I.447) is DENIED.
4. PharmaStem's Motion to Strike the Affidavit of Chris Adams (D.I. 487) is DENIED as moot.
5. The clerk shall enter judgment in favor of the defendants and against the plaintiff on the claim of infringement of U.S. Patent No. 5,192,553.
6. A new trial shall be held on the issue of

Not Reported in F.Supp.2d

Page 11

Not Reported in F.Supp.2d, 2004 WL 2127192 (D.Del.)  
(Cite as: Not Reported in F.Supp.2d)

infringement and damages with respect to U.S.  
Patent No. 5,004,681.

D.Del.,2004.  
PharmaStem Therapeutics, Inc. v. ViaCell, Inc.  
Not Reported in F.Supp.2d, 2004 WL 2127192  
(D.Del.)

END OF DOCUMENT

© 2007 Thomson/West. No Claim to Orig. U.S. Govt. Works.



# **EXHIBIT J**

Westlaw.

Not Reported in F.Supp.2d

Page 1

Not Reported in F.Supp.2d, 2004 WL 1562556 (E.D.Pa.)  
(Cite as: Not Reported in F.Supp.2d)

**H**

Out-A-Sight Pet Containment, Inc. v. Radio  
Systems Corp.  
E.D.Pa., 2004.

Only the Westlaw citation is currently available.  
United States District Court, E.D. Pennsylvania.  
OUT-A-SIGHT PET CONTAINMENT, INC.,  
Plaintiff

v.

RADIO SYSTEMS CORPORATION, Radio Fence  
Distributors, Inc., and Lori Volwiler, Defendants  
No. Civ.A. 01-5775.

July 9, 2004.

Alexander Ewing Jr., Gollatz Griffin & Ewing PC,  
West Chester, PA, William Dunnegan, Perkins &  
Dunnegan, New York, NY, for Plaintiff.

Joseph A. Woodruff, Terrence O. Reed, Waller,  
Lansden, Dortch and Davis, Nashville, TN, Thomas  
J. Bradley, McBreen & Kopko, Philadelphia, PA,  
Darol H.M. Carr, David A. Holmes, Farr Farr  
Emerich Sifrit Hackett & Carr PA, Punta Gorda,  
FL, for Defendants.

## MEMORANDUM

POLLAK, J.

\*1 Presently before the court in this action are a second set of motions in limine by defendants Radio Systems Corporation ("RSC"), Radio Fence Distributors, Inc. ("RFD"), and RFD president Lori Volwiler (collectively, "defendants"), to exclude the testimony of Stephen J. Scherf, the damages expert for plaintiff Out-A-Sight Pet Containment, Inc. ("OAS"). For the reasons discussed herein, defendants' motions in limine will be granted.

## Background

OAS, a now-defunct distributor of electronic pet containment equipment, filed suit against the defendants for breach of contract, interference with

existing and prospective contractual relations, and antitrust violations. OAS alleges that, induced by RFD, RSC violated a 1999 supply agreement ("Supply Agreement") with OAS when it refused to sell a programmable receiver known as model UL-275D to OAS, which intended to resell that model under its own label. Mr. Scherf intends to testify as to the damages incurred by OAS as a result of the defendants' alleged unlawful conduct.

Pursuant to Rule 26(a)(2)(B) of the Federal Rules of Civil Procedure, on July 24, 2002, Mr. Scherf prepared an expert report ("Report on Damages") providing valuations of OAS under three potential scenarios that might have occurred but for the defendants' alleged unlawful acts. Typically, a company's lost profits are calculated based largely on the company's historical revenues. Because OAS was essentially a start-up company with little historical revenue information, however, Mr. Scherf based his analysis primarily on OAS's business plans for fiscal years 2002-2006. The business plans were themselves based on sales projections for OAS made by Rich Weinssen, a former distributor for a competing pet containment company, Innotek.

In their initial motions in limine, filed June 20, 2003, the defendants challenged, *inter alia*, Mr. Scherf's reliance on Mr. Weinssen's sales projections. After holding a hearing, I issued a memorandum and order on December 3, 2003, granting in part the defendants' motions in limine. I found the sales projection for fiscal year 2002 to be sufficiently reliable to support expert testimony. In contrast, I found the sales projections for fiscal years 2003 to 2006—each of which assumed that OAS would experience an annual sales growth rate of 47 percent—to be speculative and thus incapable of supporting Mr. Scherf's damages estimates. In a subsequent conference call with the parties, I explained that Mr. Scherf could undertake to provide a reliable factual foundation to support Mr. Weinssen's sales projections for fiscal years 2003 to 2006—and, in turn, to support Mr. Scherf's own

© 2007 Thomson/West. No Claim to Orig. U.S. Govt. Works.

Not Reported in F.Supp.2d

Page 2

Not Reported in F.Supp.2d, 2004 WL 1562556 (E.D.Pa.)  
(Cite as: Not Reported in F.Supp.2d)

damages estimates-through the submission of a revised report.

On December 31, 2003, Mr. Scherf completed a supplemental expert report ("Supplemental Report"). In the Supplemental Report, Mr. Scherf offers the same damages estimates as he provided in the Report on Damages, and reiterates his opinion that the 47 percent annual sales increase projected by Mr. Weinssen was reasonable. The Supplemental Report contains three new sets of facts that purportedly support Mr. Scherf's adoption of the 47 percent figure: (1) the annual sales growth rate of RFD from 1998 or 1999 to 2002; (2) the sales growth rates of Perimeter Technologies ("Perimeter"), a distributor of electronic pet containment equipment run by former OAS president John Purtell, from 2000 to 2001 and 2001 to 2002; and (3) the sales growth rates of RSC from 1993 to 1997 and from 1993 to 2002.<sup>FN1</sup>

FN1. The Supplemental Report also comprises two other new features. The first is a list of findings from "additional market research" that, according to Mr. Scherf, indicate "strong growth" in the pet containment industry. It is questionable whether these broadly stated findings in any way bolster the reliability of the 47 percent sales growth rate adopted by Mr. Scherf. In any event, in its memorandum in opposition to the motions in limine, OAS does not even mention these findings in its discussion of the "additional evidence" in the Supplemental Report supporting Mr. Scherf's estimates. See Memorandum of Plaintiff in Opposition at 4.

Second, the Supplemental Report includes a collection of more conservative damages estimates based on a range of projected sales growth rates from 0 percent to 40 percent, calculated in 5 percent intervals. Because Mr. Scherf continues to stand by his original damages estimates, which are based on a 47 percent annual growth rate, the alternative estimates in the Supplemental Report do not assist Mr. Scherf's attempt to demonstrate a sufficient

factual foundation for his expert opinion, and are thus of little use to the fact-finder in this case.

\*2 The defendants responded on March 26, 2004, and April 1, 2004, with new motions in limine, raising four overarching challenges to the reliability and relevance of Mr. Scherf's proposed testimony: (1) that Mr. Scherf's damages estimates are still not supported by reliable underlying data; (2) that Mr. Scherf's opinion is irrelevant because it relates solely to damages that were not within the contemplation of the parties at the formation of the Supply Agreement; (3) that Mr. Scherf's opinion as to damages incurred beyond the termination of the Supply Agreement is irrelevant because such damages are not recoverable; and (4) that Mr. Scherf's opinion is irrelevant because OAS cannot recover speculative lost profits. I held a hearing on the new motions in limine on April 14, 2004, at which two witnesses testified on behalf of OAS: Mr. Scherf and Mr. Purtell.

## Discussion

When considering a challenge to expert testimony under Rules 702 and 703, the court must assess whether there are good grounds to rely on the data adduced in support of the expert's opinion. *In re Paoli R.R. Yard PCB Litigation*, 35 F.3d 717, 748-49 (3d Cir.1994). For an expert's testimony to be admitted, his assumptions must be "accompanied by a sufficient factual foundation." *Gumbs v. Int'l Harvester, Inc.*, 718 F.2d 88, 98 (3d Cir.1983). The burden falls on the proponent of the expert testimony-here, OAS-to demonstrate by a preponderance of the evidence that the testimony is reliable. See *In re Paoli*, 35 F.3d at 744.

### 1. Reliability of underlying data

The defendants' central contention in their second motion in limine is that the Weinssen sales projections relied upon by Mr. Scherf continue to be unsupported by sufficient evidence and thus incapable of supporting expert testimony. This court must examine whether the new data supplied by Mr.

Not Reported in F.Supp.2d

Page 3

Not Reported in F.Supp.2d, 2004 WL 1562556 (E.D.Pa.)  
(Cite as: Not Reported in F.Supp.2d)

Scherf-namely, comparative sales growth figures for RFD, Perimeter, and RSC-provide sufficient support for the Weinssen sales projections as to make Mr. Scherf's reliance on those projections reasonable. The critical question is whether these three companies in the electronic pet containment industry are comparable to OAS.

The first figure cited by Mr. Scherf arises from the deposition testimony of RFD vice president Larry Volwiler, who stated that RFD had experienced growth of "50 to 100 percent per year" over a period of "[p]robably three, maybe four" years prior to the deposition in May 2002. At the hearing, Mr. Scherf testified that in preparing the Supplemental Report he had access to no RFD sales information beyond this statement by Mr. Volwiler, and conducted no independent analysis of whether, or why, RFD experienced the growth indicated by Mr. Volwiler. It is certainly conceivable that OAS and RFD might be comparable entities. Significantly, the two companies sold, or planned to sell, the same products designed by the same manufacturer, RSC. However, several factors suggest that the two companies may not be comparable-factors that were either not considered by Mr. Scherf or not addressed in his Supplemental Report. RFD's sales were national in scope, whereas OAS intended to operate only in the northeastern United States. Furthermore, it appears that RFD has sold electronic pet containment products both through its dealer network and, via the internet, directly to consumers. The burden is Mr. Scherf's to demonstrate that RFD and OAS are comparable companies, such that RFD's past sales growth rate of "50 to 100 percent per year" supports Mr. Scherf's adoption of an estimated 47 percent annual growth rate for OAS. I find that Mr. Scherf has failed to meet this burden.

\*3 Nor does the growth rate experienced by Perimeter provide support for the 47 percent figure. In his Supplemental Report, Mr. Scherf observes that Perimeter experienced approximate growth rates of 50 percent from 2000 to 2001 and 135 percent from 2001 to 2002. Perimeter's sales, however, were boosted significantly by the withdrawal of industry leader Innotek from the electronic pet containment industry in 2001, which

allowed Perimeter to sign Innotek's former dealers. Mr. Scherf concedes that such an event-the cessation of business by a major competitor-was unlikely to occur on an annual basis. Accordingly, the circumstances surrounding Perimeter's growth from 2000 to 2002 do not serve as a useful comparison to the growth that OAS would likely have experienced from 2003 to 2006.

Finally, Mr. Scherf looks for support to the growth rate of RSC, whose sales grew by approximately 39 percent from 1993 to 1997 and by approximately 32 percent from 1993 to 2002. As the defendants point out, during those periods RSC operated in a different market than the one planned for OAS. Unlike OAS, which intended to operate a dealer network that would sell dealer-installed electronic fences directly to consumers, RSC primarily sold uninstalled "off-the-shelf" electronic fences to retail stores from 1993 to 2002. At the hearing, both Mr. Scherf and OAS's counsel admitted that this difference made RSC a less relevant comparison than RFD or Perimeter. I agree, and find that the comparative sales data for RSC provides no support for the calculation of OAS's estimated annual growth rate used by Mr. Scherf.

For these reasons, I continue to find an absence of "good grounds on which to find the data reliable." *In re Paoli*, 35 F.3d at 748. The three isolated pieces of sales growth data collected by Mr. Scherf in his Supplemental Report do not provide the necessary factual foundation for his adoption of Mr. Weinssen's sales projections for fiscal years 2003 to 2006.

Mr. Scherf's expert opinion, as outlined in his Supplemental Report, takes the form of damages estimates under each of three potential business paths that OAS might have taken but for the defendants' alleged unlawful conduct. His opinion as to damages incurred under all three scenarios is based, at least in part, on Mr. Weinssen's sales projections for fiscal years 2003 to 2006. The damages estimates under the first two scenarios rely in part on Mr. Weinssen's fiscal year 2003 projections, and the estimate under the third scenario relies in part on Mr. Weinssen's sales projections for fiscal years 2003 to 2006. Mr.

Not Reported in F.Supp.2d

Page 4

Not Reported in F.Supp.2d, 2004 WL 1562556 (E.D.Pa.)  
(Cite as: Not Reported in F.Supp.2d)

Scherf's damages estimates under all three scenarios are thus based, at least in part, on data that lack sufficient factual foundation. Because these damages estimates represent the core of Mr. Scherf's proposed expert testimony as embodied in his Supplemental Report, I conclude that the proposed testimony is inadmissible.<sup>FN2</sup>

FN2. Because I am excluding Mr. Scherf's proposed expert testimony on the first ground raised by the defendants—that his damages estimates are not supported by reliable underlying data—I do not address the remaining challenges to Mr. Scherf's testimony raised in the motions in limine.

#### Conclusion

Accordingly, in the accompanying order, I will grant the defendants' motions in limine to exclude Mr. Scherf's proposed expert testimony.

#### ORDER

\*4 For the reasons stated in the accompanying memorandum, it is hereby ORDERED that:

(1) Radio Systems Corporation's Motion for Leave to File Reply Memorandum (Docket # 94) is GRANTED.

(2) The motions of Radio Systems Corporation (Docket # 90) and of Radio Fence Distributors, Inc. and Lori Volwiler (Docket # 91) to exclude the testimony of Stephen J. Scherf are GRANTED, and it is ORDERED that Mr. Scherf will not testify as proposed in his Supplemental Report.

E.D.Pa., 2004.

Out-A-Sight Pet Containment, Inc. v. Radio Systems Corp.

Not Reported in F.Supp.2d, 2004 WL 1562556 (E.D.Pa.)

END OF DOCUMENT

# EXHIBIT K



**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**

# **EXHIBIT L**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**

# **EXHIBIT M**

**THIS EXHIBIT HAS BEEN  
REDACTED IN ITS ENTIRETY**